

**Center for Air Toxic Metals**  
*Organized and Administered through the*  
**University of North Dakota**  
**Energy & Environmental Research Center**



**1996-97 Annual Report**  
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College of Arts and Sciences  
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College of Business and Public Administration  
Department of Finance

Center for Aerospace Sciences  
Computer Science

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Northern States Power Company  
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## *CATM AT A GLANCE*

The Center for Air Toxic Metals (CATM) at the University of North Dakota (UND) Energy & Environmental Research Center (EERC) was established in 1992 by the U.S. Environmental Protection Agency (EPA) Office of Environmental Engineering and Technology Demonstration (OEETD) to focus national research efforts addressing air toxic trace element emissions, which have become a matter of worldwide concern as well as a regulatory issue in the United States.

To support EPA, CATM provides a nationally coordinated and practically oriented multidisciplinary research, development, and training program on the prevention, transformation, behavior, and control of potentially toxic metal emissions from energy-producing and incinerating systems and on the prevention and minimization of the effect of these metals on the environment through partnerships developed with industry, research institutions, and government.

The goal of CATM is to develop key information on air toxic metal compounds such that pollution prevention strategies can be developed and implemented to reduce air toxic metal emissions. Specific objectives of CATM are to 1) elucidate air toxic transformation mechanisms and pathways in energy-producing and incinerating systems, 2) develop and demonstrate technologies to control metals behavior and emissions, 3) develop and demonstrate environmentally sound methods to utilize and dispose of residuals, 4) develop and validate methods to sample and analyze air toxics, 5) develop

predictive tools and databases, 6) develop partnerships with industry, 7) develop environmental awareness and pollution prevention programs through education, and 8) commercialize results and technologies.

To accomplish the mission and goals of CATM, new partnerships and existing relationships with government, industry, and research institutions are encouraged. CATM is the focal point of these partnerships that are key to effective research and development programs.

CATM is organized into five integrated program (focus) areas. Program Area 1 – Air Toxic Metals Transformation Mechanisms focuses on the determination of the chemical and physical transformations of air toxic metals as a function of the association and abundance of the metal in fuel and system design and operating conditions. Program Area 2 – Analytical Methods Development involves the verification and enhancement of existing methods and application of new methods to effectively speciate and determine the abundance of air toxic metals in fuels and process streams. Program Area 3 – Control Technologies focuses on pollution prevention and evaluating and enhancing currently used emission control technologies for air toxic trace elements. In addition, efforts are made to identify new methods to prevent and control emissions based on a more fundamental understanding of the transformation mechanisms determined in Program Area 1. Program Area 4 – Modeling and Database Development involves the development of

tools to predict the fate of air toxic metals in combustion, gasification, and incineration systems. This task utilizes information generated in Program Areas 1-3 in the development of models and databases. In turn, these models and databases will be used for experimental design and identification of opportunities to prevent and control metal emissions. Program Area 5 – Technology Commercialization and Education involves the development of partnerships through the transfer of information from CATM to industrial sponsors as well as to academic and government partners through newsletters, education programs, and annual meetings. Timely exchange of up-to-date information is critical for health risk assessments, setting regulatory standards, and developing control strategies.

The needs of both industry and government are addressed through the CATM organization and established infrastructure. Funding from other sources complements and extends the scope of the base program. The distribution of funds among the five program areas is shown in the accompanying graph.

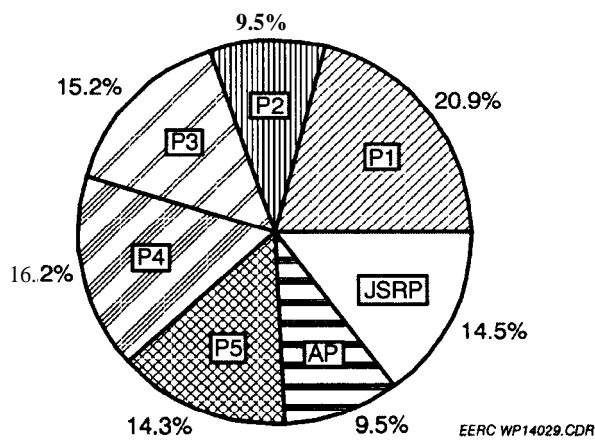
To encourage industry participation, over 20% of the CATM funds are set aside to perform research projects with industry. Specific projects involving aspects of air toxic metals of interest to industry can be jointly funded to be cost-shared with industry; 14.5% of funds are set aside for these Jointly Sponsored Research Program (JSRP) projects.

These projects must fit within the mission and goals of CATM; each project is approved on a case-by-case basis. An additional 9.5% is contributed by industrial sponsors through the

CATM Affiliates Program. These funds are designated for research projects that address specific concerns or interests of the Affiliates Program sponsors.

### Center for Air Toxic Metals

#### 1996-1997 Distribution of Funds



- |              |  |
|--------------|--|
| <b>P1:</b>   | <b>Program Area 1 – Air Toxic Metals Transformation Mechanisms</b> |
| <b>P2:</b>   | <b>Program Area 2 – Analytical Methods Development</b>             |
| <b>P3:</b>   | <b>Program Area 3 – Control Technologies</b>                       |
| <b>P4:</b>   | <b>Program Area 4 – Modeling and Database Development</b>          |
| <b>P5:</b>   | <b>Program Area 5 – Technology Commercialization and Education</b> |
| <b>AP:</b>   | <b>Affiliates Program</b>  |
| <b>JSRP:</b> | <b>Jointly Sponsored Research Program Projects</b>                 |

### *CATM DIRECTOR'S REPORT*

CATM at UND's EERC is the focal point of research directed toward minimizing the impact of air toxic metals on the environment. Through its partnerships, CATM continues to address critical questions concerning health risks, toxic metal transformations and pathways, sampling and measurement of toxic metal emissions, and related toxic metal control technologies. Over the past several years, a significant amount of research has focused on hazardous air pollutants (HAPs), specifically mercury (Hg). In December 1997, the Mercury Report to Congress was released, and in February 1998, the Study of Hazardous Air Pollutant Emissions from Electric Utility Steam Generating Units – Final Report to Congress was released. As highlighted in these reports, additional research is needed on air toxic metals:

- Additional source test data from a number of source categories.
- Additional data on the fundamental mechanisms responsible for conversion of Hg to other chemical species and the natural adsorption of Hg with the native fly ash as a result of combustion of certain coals or postcombustion conditions.
- Development and validation of improved Hg emission measurement and monitoring protocols and methods.
- Development and commercialization of more cost-effective control technologies.



*CATM Director, Dr. Steven A. Benson*

- Determination of reemitted Hg from disposal of energy conversion waste by-products.
- Improved modeling capabilities for predicting Hg speciation, conversion, adsorption with fly ashes and sorbents, control effectiveness, and the different forms potentially emitted; local and regional atmospheric fate and transport models.
- Better access by the general public to information concerning HAP emissions from power plants.

Through the CATM program, many of these research areas are or will be addressed.

### ***Current Research Activities***

***Process Impacts on Trace Element Speciation.*** This project is focused on factors that influence the speciation of Hg in combustion flue gases. The speciation of Hg is an important factor since it has a significant impact on the effectiveness of control technologies and its transport in the environment if emitted. Hg exists primarily as gaseous elemental mercury,  $\text{Hg}^0(\text{g})$ , and as gaseous or solid inorganic mercuric compounds,  $\text{Hg}^{2+}\text{X}$  (where X is  $\text{Cl}_2[\text{g}]$ ,  $\text{SO}_4[\text{s}]$ ,  $\text{O}[\text{s,g}]$ , etc.), in coal combustion flue gas. Chlorine and ash particulate, which are common flue gas constituents, can have profound impacts on Hg speciation. The primary goal of this year's work was to determine whether chlorination is a dominant Hg transformation mechanism in a real coal combustion flue gas. A secondary goal was to identify the flue gas components and mechanisms accountable for the apparently enhanced Hg sorption characteristics of coal fly ash.

***Novel Approaches for Prevention and Control of Trace Metals.*** The prevention and control of HAPs are being explored through beneficiation of the fuel. A precombustion process that removes trace metals, chlorine, and other HAP air pollutant precursors from the fuel and/or waste prior to conversion using hydrothermal treatment shows promise.

***Development and Demonstration of Trace Metals Database.*** The CATM database has been established to facilitate public access to information and research on the prevention, transformation, behavior, and control of toxic metal emissions from energy-producing and

incineration systems. The primary applications of the database are to aid in the development of methods to predict the fate of metals in fossil fuel systems, determine the effectiveness of control devices, and assist in identifying new control technologies. The database provides an interactive user application from which users can efficiently access and display information relevant to their particular need or area of concern. The data are maintained in a relational database engine at the EERC, which is accessible through the Internet.

***Nickel Speciation from Residual Oil Ash.*** The speciation of nickel (Ni) emitted from residual oil-fired utility boilers requires investigation because the possible presence of respirable particles containing nickel subsulfide ( $\text{Ni}_3\text{S}_2$ ) is a health concern. An experimental approach was used to investigate the Ni speciation of residual oil combustion ash.

***Atmospheric Deposition: Air Toxics at Lake Superior.*** CATM personnel are actively participating in discussions related to determining the fate of Hg in the Lake Superior region. This effort has included a number of state and federal agencies as well as several universities and industry representatives. Information has been provided by CATM to this project as a result of literature searches on receptor/deposition modeling, the use of tracers for point-source emissions, and mercury cycling in lakes. Discussions and information transfer with all team members have contributed to development of an approach to predict how reductions in Hg emission from thermal sources will impact the bioavailability of Hg in fish.

***Development of Speciation and Sampling Tools for Mercury in Flue Gas.*** Construction of a sampling probe has been completed and tested; work is under way to incorporate a particulate removal system in the probe. Experimental results indicate the ability to transport mercury-laden flue gas through the probe without affecting its speciation or concentration. The transport of Hg in flue gas is vital to the development of a viable continuous emission monitor (CEM) for mercury and to the ability to generate valid speciation data.

***Technology Commercialization and Education.*** The fourth annual CATM meeting was held at the EERC in September 1997 increasing public access to information. The purpose of the meeting was to provide a forum by which industry, government, and the research community could exchange information on air toxic metals and provide direction for CATM's research, development, and commercialization programs. Approximately 60 people participated, representing the government (including EPA, the U.S. Department of Energy [DOE], the Minnesota Pollution Control Agency [MPCA], the Wisconsin Department of Natural Resources, the U.S. Geological Survey [USGS], and the Michigan Department of Environmental Quality), industry, and academic research organizations.

#### ***Future Research Activities***

***Impacts of Coal and Biomass Inorganic Components on Mercury Speciation.*** A year-long project is proposed to investigate the inorganic components and mechanisms involved in Hg-coal fly ash interactions that

result in Hg oxidation (i.e., the formation of inorganic mercuric compounds:  $\text{Hg}^{2+}\text{X}[\text{s}, \text{g}]$ , where X is  $\text{Cl}_2[\text{g}]$ ,  $\text{SO}_4[\text{s}]$ ,  $\text{O}[\text{s}, \text{g}]$ , etc.) and Hg sorption on ash particles, i.e., the formation of particle-associated mercury ( $\text{Hg}[\text{p}]$ ).

***Development of Mercury Control Technologies.*** Cost-effective Hg control for coal-fired boilers is a primary research need identified in the recent U.S. EPA Mercury Study Report to Congress. This project addresses that primary need as well as more specific needs stated in the report. As stated in the Mercury Report, many control approaches have been tried, and more cost-effective solutions are needed. The proposed work *Task 1 - Reactive Sorbents for In-Duct Mercury Capture* is intended to develop test protocol and evaluate promising sorbents that are reactive enough to provide rapid in-duct Hg capture when injected upstream of a particulate control device. *Task 2 - Economic Evaluation of Mercury Control Options* is for the purpose of evaluating the economics of several alternatives for Hg control so that a clear path is available to help select the best available technology and to provide a benchmark from which economic improvements can be made in the future.

***Application of Databases and Models to the Fundamental and Applied Study of Air Toxic Metals.*** Enhancement of CATM database and predictive thermochemical equilibrium models has been an integral part of the CATM program at the EERC for the last 5 years. Database and modeling tools that have been developed are in place and already being accessed and employed by members of industry, academia, and government.

***Mercury Formation and Fate.*** The goal of this project is to provide information that will assist in determining the potential impact of Hg emissions from North Dakota lignite-fired power plants on the bioavailability of Hg to humans.

***Physicochemical Properties and Control of Transition Metal Emissions from Oil-Fired Utility Boilers.*** A recent EPA Office of Air Quality Planning and Standards Staff Paper summarized epidemiological studies and concluded that the increased adverse health effects noted were most closely associated with the fine particulate matter (PM) “generated largely by combustion processes.” The Staff Paper also highlighted ultrafine particles and transition metal (e.g., V, Fe, and Ni) ions as potential mechanisms for these health impacts. PM produced from the combustion of heavy fuel oils may possess characteristics of the ambient air PM fraction implicated in the adverse health effects associated with air particulate pollution. Consequently, the potential for more stringent particulate emission regulations exists for oil-fired utility boilers.

### ***HIGHLIGHTS FOR 1996-1997***

Research activities this year addressed several key issues related to air toxic metals. A summary of these research activities follows.

***Process Impacts on Trace Element Speciation.*** The focus of research this year in the area of process impacts on trace element species formation was Hg because of growing concern for the suspected adverse impacts of this element on human health. The current knowledge of Hg transformations and speciation in coal combustion flue gas is based largely on thermodynamic modeling and experimental investigations of Hg reactions in simulated flue gases and, to a limited extent, on interpretations of field test data. Hg exists primarily as gaseous elemental mercury,  $\text{Hg}^0(\text{g})$ , and as gaseous or solid inorganic mercuric compounds,  $\text{Hg}^{2+}\text{X}$  (where X is  $\text{Cl}_2[\text{g}]$ ,  $\text{SO}_4[\text{s}]$ ,  $\text{O}[\text{s,g}]$ , etc.), in coal combustion flue gas. Hg emissions from coal-fired electric utility boilers can be generally classified into three main forms: particle-associated mercury,  $\text{Hg}(\text{p})$ ; gaseous divalent mercury,  $\text{Hg}^{2+}\text{X}(\text{g})$ ; and gaseous elemental mercury,  $\text{Hg}^0(\text{g})$ . Gaseous mercuric chloride ( $\text{HgCl}_2[\text{g}]$ ) is generally considered to be the dominant  $\text{Hg}^{2+}\text{X}(\text{g})$  form based on theoretical and experimental investigations of Hg speciation in coal and waste combustion flue gases. The speciation of Hg is an important factor to consider in understanding its final fate when emitted from a source stack, since control options and transport models for Hg rely heavily on its form or species. Chlorine and ash particulate, which are common flue gas constituents, can have profound impacts on Hg

speciation. Although it is well established that fly ash particles capture Hg species, the nature of Hg-fly ash interactions is not well understood. The primary goal of this year's work was to determine whether chlorination is a dominant Hg transformation mechanism in a real coal combustion flue gas. A secondary goal was to identify the flue gas components and mechanisms accountable for the apparently enhanced Hg sorption characteristics of coal fly ash. A Powder River Basin (PRB) subbituminous coal from the Absaloka mine that reportedly produces significant proportions of  $\text{Hg}(\text{p})$  in the postcombustion environment of boilers was investigated. Apparently, the flue gas and/or fly ash produced from Absaloka coal combustion possess intrinsic properties that promote Hg-fly ash sorption. Hg sorption by fly ash can occur via physical adsorption, chemisorption, chemical reaction, or a combination of these processes. Investigations of Hg-Cl-fly ash interactions were performed using the conversion and environmental process simulator (CEPS), a 42-MJ/hr pilot-scale coal combustion system.

Gaseous elemental Hg and HCl were injected into a simple 1250°C oxygen-nitrogen gas mixture. In addition, the Absaloka coal ( $0.052 \pm 0.005$  p.m. Hg,  $50 \pm 10$  p.m. Cl) was burned at an excess  $\text{O}_2(\text{g})$  of 8.5 mol% while 50- and 100-ppmv  $\text{HCl}(\text{g})$  were injected into the furnace at 1330°C. Hg and Cl speciation analyses of the resulting flue gases were performed at 200" or 250°C. Baseline testing indicated that 50% of the elemental Hg spike was transformed to a gaseous mercuric

compound ( $\text{Hg}^{2+}\text{X}[\text{g}]$ ), possibly through a catalyzed  $\text{Hg}^0(\text{g})-\text{O}_2(\text{g})$  reaction involving a refractory metal oxide compound. Low recoveries of  $\text{Hg}^0(\text{g})$  and the formation of  $\text{Cl}_2(\text{g})$  during 1 00-ppmv  $\text{HCl}(\text{g})$  spike tests into the gas mixture suggest that  $\text{HgCl}_2(\text{s,l})$  was formed and deposited in the combustor. Baseline testing of Absaloka coal showed that about 20% of the total Hg had been converted to particle-associated mercury, with the remaining 80% being a near even proportion of oxidized and elemental gas forms. Cl analyses of the flue gas and fly ash indicate that  $\text{HCl}(\text{g})$  was scavenged by ash particles. The formation of particle-associated Cl, however, inhibited Hg-fly ash sorption. This inhibition effect is consistent with experimental investigations of lime ( $\text{CaO}[\text{s}]$ )-based sorbents for Hg and  $\text{HCl}(\text{g})$  control, thus suggesting that  $\text{CaO}(\text{s})$  is an important Hg-sorption component of Absaloka fly ash. X-ray diffraction (XRD) analysis of fly ashes were conducted to identify crystalline ash components. XRD analyses confirm that  $\text{CaO}(\text{s})$  is a major component of Absaloka fly ash.

***Novel Approaches for Prevention and Control of Trace Metals.*** Two novel technologies for prevention and control of HAPs are being explored. The first is a precombustion process that removes trace metals, chlorine, and other hazardous air pollutant precursors from the fuel and/or waste prior to incineration using hydrothermal treatment. This process has a wide range of applications, including preparation of premium-grade fuels, pollution prevention in waste incinerators, treatment of contaminated soils, and processing spent sorbents. To date,

38 small batch experiments at subcritical, steam (subcritical pressure and supercritical temperature), and supercritical conditions have been carried out on two sewage sludges (high and low levels of chlorine), refuse-derived waste (RDF), petroleum coke, and raw crude oil. An additional 18 tests have been performed on two Illinois Basin coals under the CATM JSRP with the Illinois Clean Coal Institute (ICCI). Available results from the hydrothermal treatment tests show that almost complete removal of both chlorine (~99.9%) and mercury (89.6%–99.4%) can be accomplished with the sewage sludges. For the RDF case, the mercury appears to be bound rather tightly to the inorganic fraction and remains with the solid residue, producing an organic fraction that could potentially be used as a clean-burning liquid fuel. Preliminary results from extractions with petroleum coke and crude oil showed that hydrothermal processing, even at supercritical conditions, was not sufficient to remove any of the metals from the petroleum coke. Work performed under a jointly sponsored project by CATM, DOE, and ICCI indicated that sulfur levels could be reduced to less than 0.8 wt% with over 90% reduction in mercury

The second innovative technology involves a novel application of microorganisms in a fiber-based trickle bioreactor to remove trace metals and volatile organics from the flue gas stream. This work focuses on proof of concept, rather than process optimization, to investigate the capabilities of bioreactors to remove mercury and volatile organic contaminants from airstreams. The quantities of  $\text{Hg}^{+2}$  and  $\text{Hg}^0$  that the microorganisms can take up per unit cell

mass and the breakthrough time of mercury through the bioreactor filters are being determined for use in preliminary full-scale reactor design. The biofilters have been designed and inoculated with the microorganisms. Once a viable growth is established, these biofilters will be exposed to simulated flue gas streams to determine the effectiveness.

In addition to proving the technical viability of these innovative techniques for preventing and controlling HAPs, a preliminary assessment of the economic viability will be performed and the results compared to commercially available alternatives.

***Development and Demonstration of Trace Metals Database.*** The CATM database has been established to facilitate research on the prevention, transformation, behavior, and control of toxic metal emissions from energy-producing and incineration systems. The primary applications of the database are to aid in the development of methods to predict the fate of metals in fossil fuel systems, determine the effectiveness of control devices, and assist in identifying new control technologies. The database provides an interactive user application from which users can quickly and efficiently access and display information relevant to their particular need or area of concern. The data are maintained in a relational database engine at the EERC, which is accessible through the Internet.

Efforts this year focused on four major areas: 1) collection and entry of data from bench-, pilot-, and full-scale systems; 2) initial development for integration of a geographical

information system (GIS) with the CATM database; 3) the addition of a control technology's efficiency indexing algorithm; and 4) continued thermodynamic database development and enhancement.

***Nickel Speciation of Residual Oil Ash.*** The speciation of nickel (Ni) emitted from residual oil-fired utility boilers requires investigation because the possible presence of small respirable particles containing nickel subsulfide ( $\text{Ni}_3\text{S}_2$ ) is a health concern. An experimental approach was used to investigate the Ni speciation of residual oil combustion ash. Ash from a low- and high-sulfur (0.33 and 1.80 wt%, respectively) residual oil was produced using a laboratory-scale combustion system at excess oxygen ( $\text{O}_2$ ) concentrations of  $\leq 1$  and 2 or 3 mol%. Ni speciation analyses were performed using x-ray absorption fine structure (XAFS) spectroscopy, sequential extraction-anodic stripping voltammetry (ASV), and carbon paste electrode voltammetry (CPEV). XAFS measurements indicate that >95% of the total Ni present in the ashes occurs as  $\text{Ni}^{2+}$  coordinated to  $\text{O}^{2-}$ . All methods indicate that  $\text{NiSO}_4$  is the dominant form, although significant proportions of NiO (5% to 24%) were measured by sequential extraction-ASV. The sequential extraction-ASV method also indicated the presence of very small proportions, <2%, of nickel sulfide. Analyses of a high-sulfur oil ash sample and the extraction residues from this ash by CPEV suggest that the Ni sulfide is present as NiS and not  $\text{Ni}_3\text{S}_2$ . Fuel sulfur content did not significantly affect Ni speciation; however, increasing excess  $\text{O}_2$  concentrations promoted Ni sulfation. The predominance of  $\text{NiSO}_4$  and relatively low

proportions of Ni sulfide in the experimentally produced ashes are inconsistent with sequential extraction-ASV determinations of Ni speciation in ashes collected from utility-scale boilers. Differences in sampling procedures and combustion conditions are being investigated to explain this inconsistency. This ongoing research project is being supported by a consortium of Amerada Hess Corporation, American Petroleum Institute, Electric Power Research Institute (EPRI), Empire State Electric Energy Research Corporation, Florida Power & Light Company (FPL), Hawaiian Electric Company, and Public Service Electric and Gas Company.

***Atmospheric Deposition: Air Toxics at Lake Superior.*** CATM personnel have actively participated in discussions and development of a large project to determine the fate of mercury in the Lake Superior region. This project will include a number of state and federal agencies as well as several universities. Information has been provided by CATM to this project as a result of literature searches on receptor/deposition modeling, the use of tracers for point source emissions, and mercury cycling in lakes. Discussions and information transfer with all team members have contributed to development of a research plan that will provide the best possible approach to be able to predict how reductions in mercury emission will impact the bioavailability of mercury in fish.

Once this project is under way, the TraceTran models that have been developed as part of CATM will be refined based on the data that will be collected at several power plants. The results from this model will then be

linked to the atmospheric deposition modeling that will be done simultaneously.

***Development of Speciation and Sampling Tools for Mercury in Flue Gas.*** Construction of a sampling probe has been completed and tested; work is under way to incorporate a particulate removal system in the probe. Experimental results indicate the ability to transport mercury-laden flue gas through the probe without affecting its speciation or concentration. The transport of mercury in flue gas is vital to the development of a viable CEM for mercury and to the ability to generate valid speciation data. Speciation data also require an analytical method that will give accurate determinations of oxidized and elemental mercury levels. One potential method is cryogenic trapping. Research efforts to date have shown that mercuric chloride and elemental mercury can be trapped cryogenically and analyzed by atomic fluorescence. Work is under way to design and build a trap that will separate the oxidized mercury, the elemental mercury, and the flue gas components. Once the trap has been tested at the bench-scale level, a completed unit will be used for pilot-scale measurements.

***Addition of a Wet Scrubber System for Incorporation into the CEPS Flue Gas Cleanup System.*** A state-of-the-art intermediate-scale CEPS has been constructed to provide an extremely well-controlled system for determining the impacts of combustion conditions and fuel properties on toxic element speciation and control. Currently, the CEPS can only test the control and behavior of trace elements across a baghouse. The behavior of metals in wet-scrubbing systems needs to be

addressed under closely controlled conditions. This project involved the design, construction, and testing of a wet-scrubbing system for the CEPS. The goal of the proposed project is to develop improved methods to control the capture of toxic trace metal species by wet-scrubbing the flue gas generated by the combustion of selected coals.

***Technology Commercialization and Education.*** The fourth annual CATM meeting was held at the EERC in September 1997. The purpose of the meeting was to provide a forum by which industry, government, and the research community could exchange information on air toxic metals and provide direction for CATM's research, development, and commercialization programs. Approximately 60 people participated, representing the government (including EPA, DOE, the MPCA, the Wisconsin Department of Natural Resources, the USGS, and the Michigan Department of Environmental Quality), industry, and academic research organizations. Highlights of the meeting included a presentation by Martha Keating of EPA on the status of the "Mercury Report to Congress" and a panel discussion entitled "Mercury Regulations - What Are the Options?" One of the major results of the discussion was the recognition that no cost-effective control technologies are currently available for utility applications to control elemental Hg.

Two issues of the *CATM Newsletter* were published and distributed to industry and other interested parties. The newsletter is circulated within all states of the United States and to over 40 countries internationally. The

newsletter is designed to inform interested parties of air toxic issues and CATM activities and to encourage further participation and collaboration among industry and government. The newsletter is also available through the EERC's home page on the World Wide Web at [www.eerc.und.nodak.edu](http://www.eerc.und.nodak.edu).

### ***PROJECT SUMMARIES FOR 1996-1997***

The following table entitled "CATM Project Listing" summarizes the projects currently funded through CATM. These projects include those funded solely from EPA, JSRP projects cofunded by industry, and the Affiliates Program funded by industry participants. The subsequent table entitled "Listing of Related Projects on Air Toxic Metals" lists other projects conducted by the EERC related to trace metals.

#### ***CATM Project Listing***

<b>Principal Investigator</b>	<b>Project Title</b>	<b>End Date</b>	<b>1996-97 Budget</b>
<b>Funded Through CATM Base Program</b>			
Chris Zygarlicke	Process Impacts on Trace Metal Speciation	9/30/98	\$540,000
John Pavlish	Education and Commercialization	9/30/98	\$200,000
Bruce Folkedahl	Development and Demonstration of Trace Metals Database	9/30/98	\$160,000
Total			\$900,000
<b>Funded Through CATM JSRP</b>			
Mike Mann	Organic Sulfur and HAP Removal from Coal with Subcritical Water <sup>1</sup>	12/31/97	\$547,000
Kevin Galbreath	Nickel and Arsenic Speciation of Residual Oil Fly Ash <sup>2</sup>	9/30/98	\$10,000
Dennis Laudal	Linking Point-Source Emissions and Atmospheric Deposition Models	9/30/98	\$100,000
Total			\$657,000
<b>Funded Through Affiliates Program</b>			
Chris Zygarlicke	Wet Scrubber System for Incorporation into CEPS Flue Gas Cleanup System	9/30/98	\$140,000
Kevin Galbreath	Nickel and Arsenic Speciation of Residual Oil Fly Ash <sup>2</sup>	9/30/98	\$130,000
Jeff Thompson	Development of Speciation and Sampling Tools for Mercury in Flue Gas	9/28/98	\$120,000
Steve Benson/ Charlene Crocker	Environmental Training	9/28/98	\$25,000
Total			\$415,000
Total for CATM-Funded Activities			\$1,972,000

<sup>1</sup> \$290,000 from ICCI, \$100,000 from U.S. EPA, and \$157,000 from U.S. DOE.

<sup>2</sup> Funding for these projects: \$10,000 from U.S. EPA, \$60,000 from Affiliated Program, \$70,000 from industry.

***Listing of Related Projects on Air Toxic Metals***

<b>Project Title</b>	<b>Funding Sources/ End Date</b>	<b>Total Budget</b>
Mercury Emissions from North Dakota Lignite-Fired Power Plants on the Bioavailability of Mercury to Humans	DOE-NDIC <sup>1</sup> -Industry/ 1999	\$400,000
Strategic Studies	DOE/ 1997	\$42,936
Environmental Technology Systems Engineering and Cost Savings Analysis	WPI <sup>2</sup>	\$95,050
Evaluate the Fate and Distribution of Trace Elements in Integrated Gasification Systems	DOE-METC/1998	\$1,250,520
Impacts of Agricultural Chemicals on Groundwater in the Northern Great Plains	USDA <sup>3</sup> /2000	\$154,124
Subcritical Water Extraction of Mercury from Soils	DOE/ 1997	\$40,000
Formal Evaluation of Chemical Measurement Methods: Mercury Speciation Measurements in Coal Combustion Systems	DOE-EPRI/1997	\$3,111,335
Hot-Gas Filter Cleanup and Testing of Trace Elements	DOE/ 1997	\$2,672,813
Review and Assessment of Results from the Comprehensive Characterization of Air Toxic Emissions from Coal-Fired Power Plants	DOE/ 1997	\$700,000
Sorbent Development for Mercury Control	DOE/ 1997	\$255,000
Potential to Control Mercury from Coal-Fired Boilers by Using Sorbents	DOE-EPRI/1998	\$1,789,450
Advanced Hybrid Particulate Collector <sup>4</sup> , A New Concept for Air Toxics and Fine-Particulate Control	DOE-Gore/ 1999	\$1,495,646
Mercury Speciation/Capture	DOE/ 1997	\$160,000
Mercury Vapor Flux Measurements	PTI <sup>5</sup> / 1997	\$27,571
Fate and Transport of Trace Elements in Groundwater	DOE-GRI <sup>6</sup> /1997	\$800,000
Recovery of Mercury from Contaminated Primary and Secondary Liquid Wastes	ADA Technologies/ 1997	\$294,192
Environmental Management Technology Demonstration and Commercialization	DOE/ 1998	\$4,380,407
Total for Related Projects		\$17,669,044

<sup>1</sup> North Dakota Industrial Commission.<sup>2</sup> Waste Policy Institute.<sup>3</sup> U.S. Department of Agriculture.<sup>4</sup> AHPC.<sup>5</sup> PTI Environmental Services, Inc.<sup>6</sup> Gas Research Institute.

## ***RESEARCH PROJECT DESCRIPTIONS***

### **PROCESS IMPACTS ON TRACE ELEMENT SPECIATION**

Christopher J. Zygarlicke (EERC), Grant L. Schelkoph (EERC), Stanley J. Miller (EERC), Kevin C. Galbreath (EERC), Michael D. Mann (EERC)

#### ***Project Description***

The focus of research this year in this project is on the fundamental transformations of trace element species during coal combustion (Program Area 1), with a heavy emphasis on mercury interactions with ash particulate and chlorine. Bench- and pilot-scale combustion testing and advanced sampling and analytical techniques (Program Area 2) were used for experimental studies. Many of the mechanisms of trace element transformation apply to other conversion and combustion systems such as **gasifiers** and waste incinerators. The information generated is being logged into the CATM Database (Program Area 4), and the experimental data are also being compared with predictive modeling of the formation of mercury and other trace element species in combustion environments. Trace element speciation results are being applied to the development of sorbents and control technologies (Program Area 3) [1, 2]. Results of this research on mercury interactions with five gas particulate and gaseous chlorine species were presented at the CATM Fourth Annual meeting and will be presented in the 1998 Air and Waste Management Association conference in San Diego.

#### ***Goal***

The primary goal is to examine the fundamental trace metal transformation mechanisms that occur during fuel conversion. The main objectives for this year's work are as follows:

- *Trace metal modes of occurrence in coal.* Collaborative research on the mode of occurrence of (species, form, mineral associations) trace elements in coal is being performed in conjunction with a team of international laboratories.
- *Fuel and process impacts on mercury speciation and partitioning.* A focused study of the interactions of Hg with flue gas particulate and chlorine gas species and impacts on Hg speciation is being accomplished in this year's work.
- *Model predictions of trace element partitioning.* A model formulated under other project work at the EERC for prediction of gasification trace element partitioning by vapor and particulate association is being refined and tested for applications in combustion systems.

### ***Rationale***

The form and quantity of trace elements emitted from a fuel energy conversion system are a function of the trace element concentrations, forms, and associations in the fuel; the conversion process; and operating conditions. Trace element modes of occurrence have a great bearing on coal-cleaning effectiveness and possibly on the overall combustion transformation mechanisms for certain elements. Arsenic that is associated with an arsenopyrite mineral in a coal pyrite grain may react and transform in its environment differently from arsenic associated with a clay minerals as an accessory. Several elements are being considered in an international study of trace element modes of occurrence.

The main focus of research this year was in the area of process impacts on Hg speciation. The speciation of Hg is an important factor to consider in understanding its final fate when emitted from a power plant stack, since control options and transport models for Hg rely heavily on its form or species. Chlorine and ash particulate, which are common flue gas constituents in coal combustion flue gas, can have profound impacts on Hg speciation. Hg exists primarily as gaseous elemental species,  $\text{Hg}^0(\text{g})$ , and as gaseous or solid inorganic mercuric compounds,  $\text{Hg}^{2+}\text{X}$  (where X is  $\text{Cl}_2[\text{g}]$ ,  $\text{SO}_4[\text{s}]$ ,  $\text{O}[\text{s,g}]$ , etc.), in coal combustion flue gas. Hg emissions from coal-fired electric utility boilers can be generally classified into three main forms: particle-associated mercury,  $\text{Hg}(\text{p})$ ; gaseous divalent mercury,  $\text{Hg}^{2+}\text{X}(\text{g})$ ; and gaseous elemental mercury,  $\text{Hg}^0(\text{g})$ . Gaseous mercuric chloride ( $\text{HgCl}_2[\text{g}]$ ) is generally considered to be the dominant  $\text{Hg}^{2+}\text{X}(\text{g})$  form based on theoretical and experimental investigations of Hg speciation in coal and waste combustion flue gases.

Accurate prediction of Hg speciation and partitioning of other common trace elements is needed for devising air toxic emission control strategies, which are currently under consideration by EPA. Models are being devised in this program to predict particulate and gaseous trace element emissions during combustion.

### ***Approach***

Trace element mode of occurrence in an Illinois No. 6 coal is being identified using a combination of direct and indirect analytical techniques for determining the trace element forms and associations. Scanning electron microscopy (SEM) and wavelength-dispersive spectroscopy (WDS) were used to selectively examine mineral grains in the coal. Float-sink fractions of ground coal were analyzed using standard chemistry analytical techniques such as atomic absorption spectroscopy (MS) and x-ray fluorescence (XRF). The WDS analysis gave direct association of mineral-bound trace elements and the float-sink analysis gave more of a general inorganic or organic/fine mineral differentiation.

Mercury speciation tests were performed using a subbituminous PRB Absaloka coal ( $0.052 \pm 0.005$  ppm Hg,  $50 \pm 10$  ppm Cl) that was burned at an excess  $\text{O}_2(\text{g})$  of 8.5 mol%, while

50- and 100-ppmv HCl(g) were injected into the furnace at 1330°C. Apparently, the flue gas and/or fly ash produced from Absaloka coal combustion possess intrinsic properties that promote Hg-fly ash sorption. Absaloka was also known to have a history of producing more elemental Hg as a vapor compared to oxidized Hg vapor forms. A simple heated oxygen-nitrogen gas mixture with injections of gaseous elemental Hg and HCl was also employed to check the impacts of the reactor alone on Hg speciation. Hg and Cl speciation analyses of the resulting flue gases were performed at 200° or 250°C using the Radian International method for multimetals collection and Hg speciation. An on-line Hg analyzer was employed to check the transformation of Hg. Baghouse fly ash was also sampled and analyzed for Hg and chlorine bulk quantities. X-ray diffraction analysis of fly ashes were conducted to identify crystalline ash components using methods described by McCarthy and Solem [3].

Combustion testing using an Illinois No. 6 coal, for which other collaborating data are abundantly available, produced flue gas particulate and vapor trace element species that were partitioned by size and analyzed for trace element concentrations. The data will be compared to predictive modeling results using a modified model called TraceTran. The TraceTran model that already exists at the EERC for gasification systems predicts trace element concentrations as vapor and as particulate forms in various size fractions.

### *Progress*

#### **Trace Element Mode of Occurrence Studies**

A collaborative research effort is under way between the EERC, the USGS, the University of Kentucky, the University of Sheffield (United Kingdom), Imperial College (United Kingdom), CSIRO (Commonwealth Scientific Industrial Research Organization, Australia), BGS, CSIC (Spain), and the Geological Survey of Canada to determine the mode of occurrence of Hg, Se, As, Cd, Pb, Cu, Ni, Sb, Cr, and Zn. It is up to the collaborating laboratory to devise analytical methods determining the modes of occurrence. SEM-WDS analysis of Illinois No. 6 coal shows relative high concentrations of Hg, Ni, Cu, Se, and As in pyrite grains in the coal. Antimony and Cr show pyrite associations as well, but to lesser degrees, and they show some associations with clay and quartz particles. Sink fractions show enrichments of trace elements that have typical sulfide or clay associations. Chemical fractionation work is now being performed to determine organic associations of trace elements.

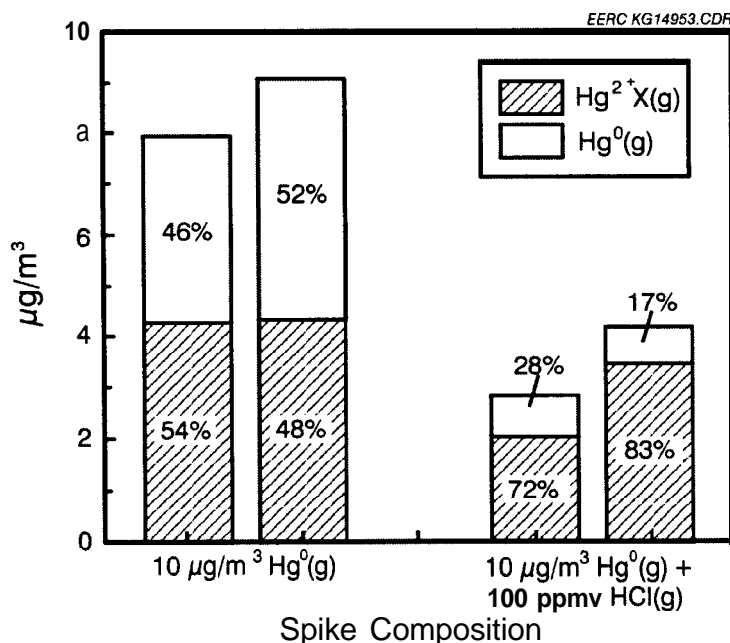
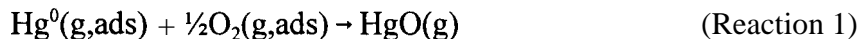
#### **Process Impacts on Mercury Speciation**

The primary goal of this investigation was to determine whether chlorination is a dominant Hg transformation mechanism in a real coal combustion flue gas. A secondary goal was to identify

the flue gas components and mechanisms accountable for the apparently enhanced Hg sorption characteristics of Absaloka coal fly ash.

### Spike Testing Using $\text{Hg}^0(\text{g})$ and $\text{HCl}(\text{g})$

The spiking of  $10 \mu\text{g}/\text{m}^3 \text{Hg}^0(\text{g})$  into a simple gas mixture of 8.5 mol%  $\text{O}_2$  and 91.5 mol%  $\text{N}_2$  indicated that about 50% of the  $\text{Hg}^0(\text{g})$  spike was transformed to  $\text{Hg}^{2+}\text{X}(\text{g})$  (see figure below). On-line analyzers indicated that the only gaseous components available to react with  $\text{Hg}^0(\text{g})$  were 8.5 mol%  $\text{O}_2$  and 30 ppmv  $\text{NO}_x$ . Kinetic limitations preclude any significant homogeneous  $\text{Hg}^0(\text{g})-\text{O}_2(\text{g})$  or  $\text{Hg}^0(\text{g})-\text{NO}_x(\text{g})$  reactions to account for the formation of  $\text{Hg}^{2+}\text{X}(\text{g})$  [4–7]. The formation of  $\text{Hg}^{2+}\text{X}(\text{g})$  must, therefore, involve a heterogeneous or catalytic reaction on ceramic or refractory surfaces in the CEPS. Possible reaction products in the Hg-NO<sub>x</sub> system include Hg nitrite and nitrate compounds, but they are generally unstable at flue gas temperatures,  $>200^\circ\text{C}$ , upstream of the sampling location [8, 93]. Alternatively, the oxidation of  $\text{Hg}^0(\text{g})$  could involve a heterogeneous reaction with adsorbed (ads)  $\text{Hg}^0$  or  $\text{O}_2$  on surfaces or a catalyzed  $\text{Hg}^0(\text{g})-\text{O}_2(\text{g})$  reaction resulting in  $\text{HgO}(\text{g})$  (decomposes at  $500^\circ\text{C}$ ) as the reaction product. The most plausible reaction is:



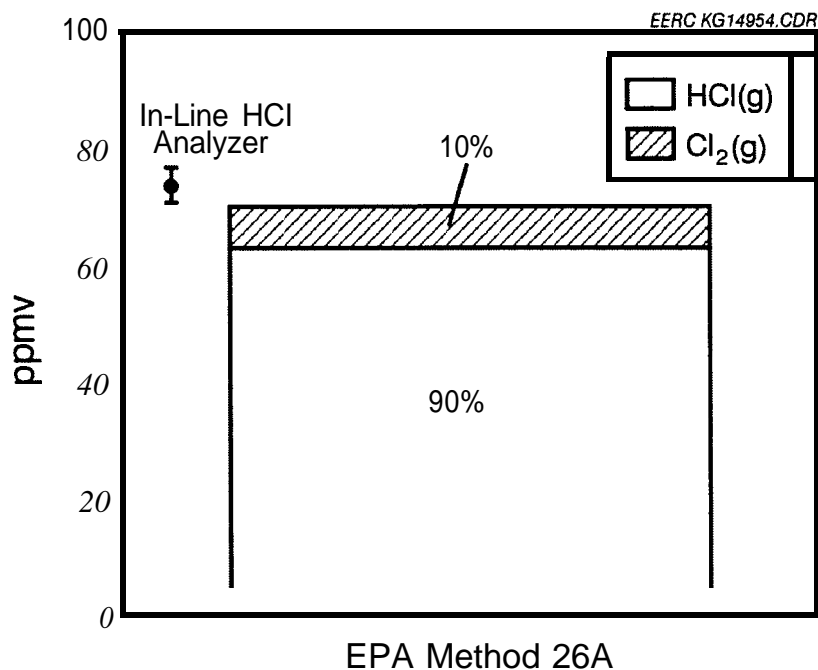
*Duplicate Hg Speciation Results for the  $10\text{-}\mu\text{g}/\text{m}^3 \text{Hg}^0(\text{g})$  Baseline Spike and  $10\text{-}\mu\text{g}/\text{m}^3 \text{Hg}^0(\text{g}) + 100\text{-ppmv HCl}(\text{g})$  Spike Tests. The relative proportions of different Hg species are indicated within each bar as a percentage of the total Hg.*

The formation of  $\text{HgO(g)}$  occurs within a temperature range corresponding to the flue gas sampling and  $\text{HgO(g)}$  decomposition temperatures, i.e., 200° to 500°C. These temperature conditions exist over a 1.85-m refractory-lined section of the CEPS upstream of the sampling location. Flue gas residence time in this section is estimated to be <0.1 s. Hall and others [4] experimentally investigated the heterogeneous reaction of  $\text{Hg}^0(\text{g})$  with  $\text{O}_2(\text{g})$  in the presence of activated C and fly ash at 20° to 700°C. They concluded that Reaction 1 was not an important heterogeneous reaction because of kinetic limitations and the relatively short residence time in a flue gas duct. An alternative explanation is that Reaction 1 is catalyzed by a component of the refractory used in the combustor. A detailed chemical and mineralogical characterization of refractory from the baghouse-inlet sampling port indicates that corundum ( $\text{Al}_2\text{O}_3$ ), mullite ( $\text{Al}_3\text{Si}_2\text{O}_7$ ), dicalcium silicate ( $\text{Ca}_2\text{SiO}_4$ ), anhydrite ( $\text{CaSO}_4$ ), and rutile ( $\text{TiO}_2$ ) compose the refractory. The  $\text{CaSO}_4$  component is actually present as an irregular white coating on the refractory surface and is not an essential refractory component.  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  are known catalysts; however, additional laboratory-scale tests are required to evaluate whether any of these refractory components can catalyze Reaction 1.

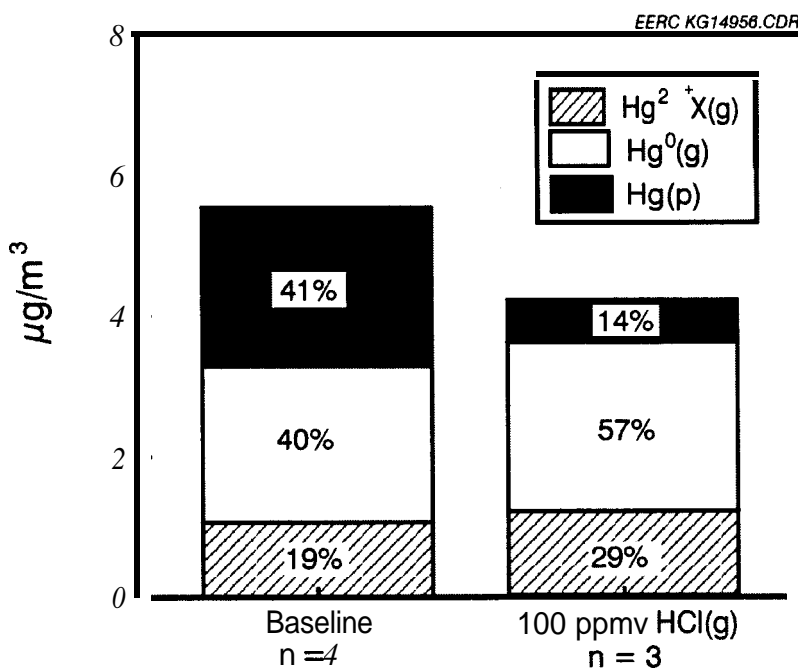
Poor recoveries of  $\text{Hg}^0(\text{g})$  during the 1 0- $\mu\text{g}/\text{m}^3$   $\text{Hg}^0(\text{g})$  + 1 00-ppmv  $\text{HCl}$  spike test (see figure on page 22) provide indirect evidence for the formation of  $\text{HgCl}_2(\text{s,l})$  (melting point 276°C, boiling point 302°C). Apparently, the formation of  $\text{HgCl}_2(\text{s,l})$  involves  $\text{Hg}^0(\text{g})$  as a reactant and not  $\text{Hg}^{2+}\text{X}(\text{g})$  (where X is suspected to be  $\text{O}^{2-}$ ). Cl speciation results, presented in the figure at the top of the next page, indicate that 7 ppmv of  $\text{Cl}_2(\text{g})$  was available in the gas stream to react homogeneously with  $\text{Hg}^0(\text{g})$ . Metals such as  $\text{Al}_2\text{O}_3$  are available in the CEPS to catalyze  $\text{Cl}_2(\text{g})$  formation (Reaction 1), as indicated by XRD analysis of the refractory. Poor  $\text{HCl(g)}$  spike recoveries also suggest that Cl was available on surfaces within the combustor to react heterogeneously with  $\text{Hg}^0(\text{g})$ .

### Absaloka Coal – $\text{HCl(g)}$ Spike Tests

The Absaloka coal had 7.9 wt% ash and 0.57 wt% sulfur on an as-received basis and 0.52 ppm Hg and 50 ppm chlorine on a dry basis. Hg speciation results for the baseline Absaloka coal test, shown in the figure at the bottom of the next page, are very similar to results obtained from burning the pulverized Absaloka coal in a much larger pilot-scale (580-MJ/hr) combustion system and measuring Hg speciation using several different methods. Hg speciation results are similar despite the fact that pilot-scale testing was performed at a much lower excess  $\text{O}_2(\text{g})$  concentration of 4 mol%. This suggests that excess  $\text{O}_2(\text{g})$  concentration does not significantly affect the Hg speciation of Absaloka coal combustion flue gas. Test results from both combustion systems indicate that Absaloka coal combustion flue gas and/or entrained fly ash possess intrinsic properties which promote Hg sorption as evidenced by relatively high proportions of  $\text{Hg(p)}$ .



*On-Line and EPA Method 26A Cl Analysis Results for the 10- $\mu\text{g}/\text{m}^3$  Hg<sup>0</sup>(g) + 100-ppmv HCl(g) Spike Test. Bar represents 95% confidence limits based on three HCl measurements.*



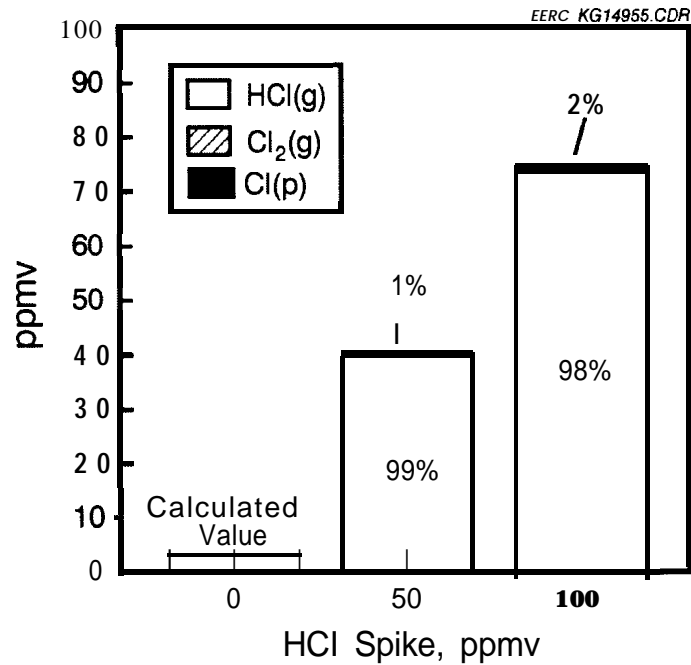
*Average Hg Speciation Results for the Absaloka Baseline and 100-ppm HCl Spike Tests. The relative proportions of different Hg species are indicated within each bar as a percentage of the total Hg.*

As seen in the following table, a significant depletion in  $\text{Hg(p)}$ , resulting in a relatively low Hg mass balance closure, provides indirect evidence for the formation of  $\text{HgCl}_2(\text{s,l})$  during the Absaloka coal + 100 ppmv-HCl spike test. Chlorine speciation measurements revealed that  $\text{Cl(g)}$  was not detected for the Absaloka coal-HCl(g) spike tests. The presence of  $\text{H}_2\text{O(g)}$  and  $\text{SO}_2(\text{g})$  apparently inhibited the formation of  $\text{Cl(g)}$ . Therefore, the formation of  $\text{HgCl}_2(\text{s,l})$  would have to involve  $\text{HCl(g)}$  or  $\text{Cl(p)}$  as a reactant.  $\text{Hg(p)}$  may have reacted heterogeneously with  $\text{HCl(g)}$  to form  $\text{HgCl}_2(\text{s,l})$  which was then deposited on surfaces within the combustor. This reaction mechanism results in the desorption of  $\text{Hg(p)}$ , implying that Hg is loosely bound to the ash. Alternatively, the presence of  $\text{HCl(g)}$  may have inhibited Hg-ash sorption and thus the formation of  $\text{Hg(p)}$ . The formation of  $\text{HgCl}_2(\text{s,l})$  would then involve a homogeneous  $\text{Hg}^0(\text{g})\text{-HCl(g)}$  or heterogeneous  $\text{Hg}^0(\text{g})\text{-Cl(p)}$  reaction. Test results, however, are inconclusive for deciphering the reaction mechanism(s) responsible for the apparent formation of  $\text{HgCl}_2(\text{s,l})$ .

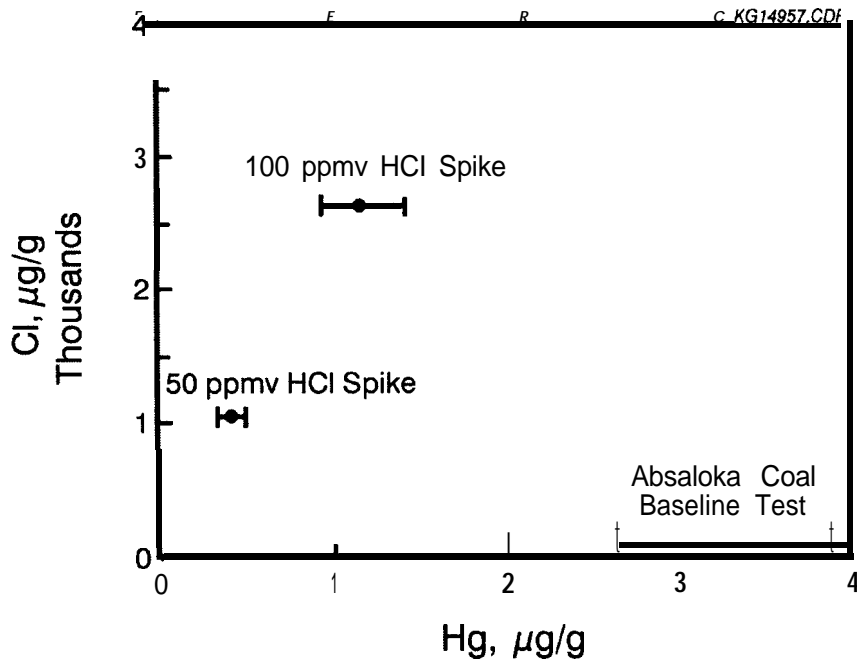
*Mercury Speciation Results for Absaloka Coal Tests*  
(mean  $\pm$  95% confidence limits,  $\mu\text{g}/\text{m}^3$ )

	Baseline	100-ppmv HCl Spike
$\text{Hg}^0(\text{g})$	$2.22 \pm 0.28$	$2.40 \pm 0.52$
$\text{Hg}^{2+}\text{X(g)}$	$1.06 \pm 0.05$	$1.21 \pm 0.11$
$\text{Hg(p)}$	$2.26 \pm 0.37$	$0.60 \pm 0.41$
Total Hg	$5.53 \pm 0.65$	$4.21 \pm 0.53$
Number of Measurements	4	3
Hg Mass Balance Closure	$110 \pm 17\%$	$82 \pm 13\%$

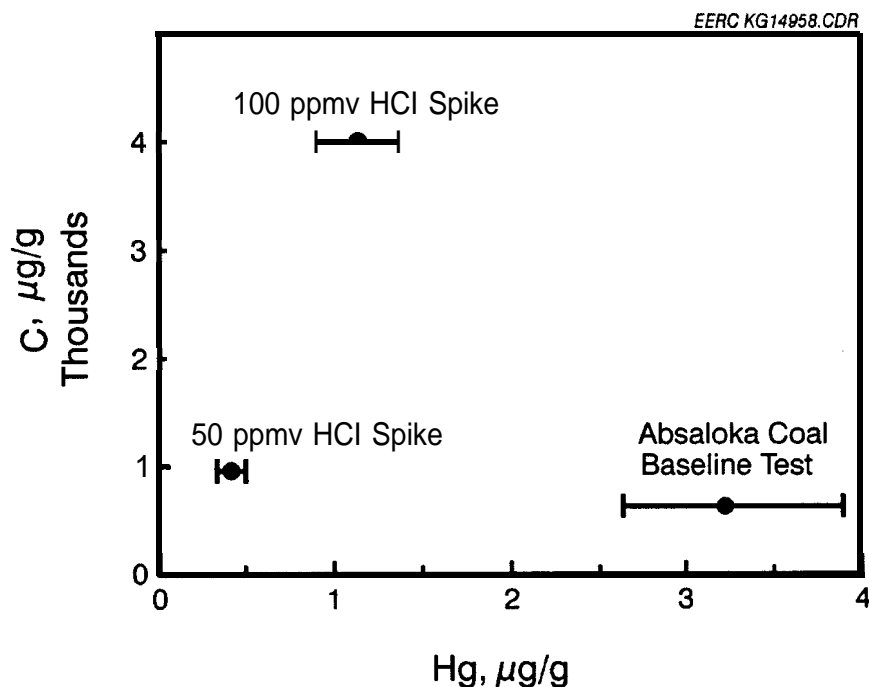
Chlorine analyses of the flue gas and collected fly ash (see figures on page 26), indicate that the injected  $\text{HCl(g)}$  is scavenged by fly ash. The lack of a positive correlation between Cl and Hg in the bottom figure on page 26 indicates, however, that the Cl retained on fly ash does not create active Cl sites for Hg chemisorption. In addition, the combination of high Cl and unburned C content of the ash produced during the 100-ppmv  $\text{HCl(g)}$  spike test (bottom figure on page 26 and figure on page 27, respectively) did not promote  $\text{Hg(p)}$  formation. Components other than chlorinated ash and C particles must promote the formation of  $\text{Hg(p)}$  in Absaloka coal fly ash. XRD analyses of baghouse ash samples were conducted to identify crystalline components that may account for the observed  $\text{Hg(p)}\text{-HCl(g)}$  interaction characteristics. Fly ash produced from Absaloka coal contains lime ( $\text{CaO}$ ) and the  $\text{CaO}$ -acid gas reaction product  $\text{CaSO}_4$  as major crystalline phases. Automated SEM analyses by Galbreath and others [10] indicate that  $\text{CaO(s)}$  is generally a major component of the fine ash fractions ( $<2\mu\text{m}$  in diameter) of PRB subbituminous coal fly ashes.  $\text{CaO(s)}$  and portlandite ( $\text{Ca}[\text{OH}]_2[\text{s}]$ ), a hydration product of  $\text{CaO(s)}$ , are effective  $\text{HgCl}_2(\text{g})$  and  $\text{HCl(g)}$  sorbents [11-13]. In bench-scale experiments, Ghorishi and Gullett [13] found that the presence of  $\text{HCl(g)}$  inhibits



*Chlorine Speciation Results for the 50- and 100-ppmv HCl(g) Injections during Absaloka Coal Combustion Tests. The baseline Cl speciation result is a calculated value.*



*Cl Versus Hg Concentrations for the Absaloka Coal Fly Ash. Bars represent 95% confidence limits based on three Hg measurements.*



*C Versus Hg Concentrations for the Absaloka Coal Fly Ash. Bars represent 95% confidence limits based on three Hg measurements.*

the adsorption of  $\text{HgCl}_2(\text{g})$  by  $\text{Ca}(\text{OH})_2(\text{s})$ . They hypothesized that this inhibition effect was a result of reactive competition for the available alkaline sites. The inverse relationship between  $\text{Hg}(\text{p})$  and  $\text{Cl}(\text{p})$  documented in this investigation is consistent with the hypothesis of Ghorishi and Gullett [13], thus implying that  $\text{CaO}(\text{s})$  is an important Hg-sorption component of Absaloka fly ash.

### Conclusions

The injection of  $10 \mu\text{g}/\text{m}^3 \text{Hg}^0(\text{g})$  into a simple heated gas mixture (8.5 mol%  $\text{O}_2$ , 91.5 mol%  $\text{N}_2$ ) indicated that as the gas cooled for approximately 2.5 s from  $1250^\circ\text{C}$  to  $200^\circ\text{C}$  about 50% of the  $\text{Hg}^0(\text{g})$  spike was transformed to  $\text{Hg}^{2+}\text{X}(\text{g})$ , where X is most likely  $\text{O}^{2-}$ . The formation of  $\text{HgO}(\text{g})$ , however, is kinetically inhibited at the relatively short residence time available in the combustor [4, 6, 7]. A catalyzed  $\text{Hg}^0(\text{g})\text{-O}_2(\text{g})$  reaction involving a refractory metal oxide compound is proposed to explain the apparent formation of  $\text{HgO}(\text{g})$ . Low recoveries of  $\text{Hg}^0(\text{g})$  during 100-ppmv  $\text{HCl}(\text{g})$  spike tests into the gas mixture suggest that  $\text{HgCl}_2(\text{s,l})$  was formed and deposited in the combustor. Cl speciation measurements indicate that  $\text{Cl}(\text{g})$ , an active Hg chlorinating agent, was available to react homogeneously with  $\text{Hg}^0(\text{g})$ .

Combustion testing of a **low-Cl** ( $50 \pm 10$  ppm) Absaloka subbituminous coal at 8.5 mol% excess  $O_2(g)$  indicated that on average 41%, 19%, and 40% of the total Hg ( $5.5 \pm 0.6 \mu g/m^3$ ) in  $250^\circ C$  flue gas was present as **Hg(p)**, **Hg<sup>2+</sup>X(g)**, and **Hg<sup>0</sup>(g)**, respectively. These results are consistent with the relatively high **Hg(p)** concentrations noted in a much larger-scale 580-MJ/hr combustion system [2], thus corroborating the enhanced Hg sorption capacity of Absaloka coal fly ash. 50- and 100-ppmv **HCl(g)** spike tests indicate that the Hg sorption capacity of Absaloka coal fly ash is adversely affected by **HCl(g)**, even though Cl is scavenged by ash particles to form **Cl(p)**. **Cl<sub>2</sub>(g)** was not detected in the coal combustion flue gas, possibly because of the inhibition effect of **H<sub>2</sub>O(g)** and **SO<sub>2</sub>(g)**. The inverse relationship between **Hg(p)** and **Cl(p)** documented in this investigation is analogous to the inhibition effect of **HCl(g)** on the **HgCl<sub>2</sub>(g)** sorption capacity of CaO-based sorbents [13]. The identification of **CaO(s)** as a dominant ash component and similarities in Hg-Cl-CaO and Hg-Cl-fly ash interactions suggest that **CaO(s)** is an important Hg-sorption component of Absaloka fly ash. Additional tests are required to confirm this hypothesis and determine whether it applies to other **PRB** subbituminous coals.

### Trace Element Transformation Modeling

The CEPS system was set up and configured to run Illinois No. 6 combustion tests with triplicate sampling of flue gas particulate and trace element forms using a five-stage multicyclone fly ash sampler and Ontario Hydro multimetals sampling train. The tests were performed flawlessly, and the ash and impinger samples were analyzed for Hg, Se, Pb, Ni, Cd, and Cr using conventional **AAS** techniques.

**TraceTran** is an EERC model that predicts the concentrations of trace elements in specific particulate size categories and in the vapor phase. The model has been adapted and modified for coal combustion systems, and the algorithms for predicting trace element concentrations in the combustion ash from coal mineral and trace element input data will be verified and calibrated using the Illinois No. 6-CEPS combustion trace element partitioning data. The results from this work were not yet available for this report.

### Status

The project was nearly completed by October 1997. The information reported here will also be included in more detail in the more comprehensive Years 4-5 CATM Final Technical Report, which covers work performed in 1996–1997. Various elements of the fundamental trace element transformation research presented here is continuing in 1998.

### ***Potential Users/Technology Transfer***

Industry and government agencies will benefit from the information and data, which will provide a greatly increased understanding of process impacts on trace element speciation. Specific users of project results are commercial vendors of particulate control devices, commercial vendors of flue gas desulfurization (FGD) systems and continuous emission monitors for air toxics, federal agencies such as the U.S. DOE and EPA, special interest and environmental groups seeking a scientific assessment of the transformations and potential fate of air toxic metals, and the general public by having access to unbiased information related to sources and potential emissions of air toxics.

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## NOVEL APPROACHES FOR PREVENTION AND CONTROL FOR TRACE METALS

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### *Project Description*

Two novel technologies for prevention and control of HAPs are being explored. The first is a precombustion process that removes trace metals, chlorine, and other HAP precursors from the fuel and/or waste prior to incineration using hydrothermal treatment. Three modes of hydrothermal treatment are being investigated during the program: subcritical water extraction, steam extraction (subcritical pressure and supercritical temperature), and supercritical water extraction. This process has a wide range of applications, including preparation of premium-grade fuels, pollution prevention in waste incinerators, treatment of contaminated soils, and processing spent sorbents. The second innovative technology involves a novel application of microorganisms in a fiber-based trickle bioreactor to remove trace metals and volatile organics from the flue gas stream. The bioreactors are novel, in that they use a polymer fiber support for the microorganisms, which improves the efficiency of removal and reduces the required quantity of cell mass required per given volume of contaminated air. In addition to proving the technical viability of these innovative techniques for preventing and controlling HAPs, a preliminary assessment of the economic viability will be performed and the results compared to commercially available alternatives.

### *Goal*

The primary purpose of this project is to demonstrate the technical viability of two novel treatment methods to simultaneously remove air toxic metals and other HAPs. While the focus of the program will be on mercury, other pollutants that should be affected by both of these processes include lead, arsenic, selenium, cadmium, chlorine, fluorine, sulfur, and volatile organics. The general goals of the program are listed briefly below, with specific objectives for each task presented with the scope of work for that task. Goals are as follows:

- To demonstrate the effectiveness of hydrothermal treatment as a pretreatment method for controlling trace metals and chlorine from medical wastes, municipal solid wastes, and other waste materials while simultaneously producing an upgraded fuel.
- To investigate the capabilities of bioreactors to remove contaminants (volatile metals and organic compounds) from airstreams using polymer fibers to support particular strains of microorganisms.

- To compare cost and effectiveness of various metal emission prevention and control technologies that are currently being researched or used commercially.

### ***Rationale***

Environmentally sound disposal of municipal and industrial wastes has become a major issue in the past decade [1, 2]. The volume of these wastes, including refuse, medical wastes, hazardous wastes, and sewage sludge has continued to grow annually, and traditional disposal methods (landfilling or ocean dumping) are becoming less acceptable because of cost and environmental concerns. Incineration in modern high-efficiency combustors is being employed for a growing fraction of waste streams to achieve significant reduction in refuse volume, but has been coupled with an increase in the complexity and efficiency of air pollution controls to limit incinerator emissions. Emission control for these systems, however, is more challenging than for a coal-fired plant because of HCl, HF, dioxin, furans, and much higher concentrations of the heavy metals (mercury, lead, cadmium, arsenic, chromium, nickel, and zinc) emissions from typical waste burning plants [3]. Consequently, precombustion technologies have an even greater potential for pollution control for waste-fired systems than for coal-fired systems.

The use of hydrothermal treatment has shown success at extracting sulfur and associated metals. Based on preliminary tests at the EERC, organically associated sulfur and metals have been extracted from coal using subcritical water; thus conditions at or above supercritical pressure may not be necessary. Work currently being conducted at the EERC under support from ICCI has confirmed that in excess of 80% of total sulfur and up to 99% of the mercury can be removed using water at 400°C and 2300 psig, much below the critical pressure of 3200 psig [4]. Other researchers have reported the beneficial extraction properties of subcritical water or hydrothermal treatment for **organics** and/or metals.

Traditional methods for air purification (adsorption, incineration, and catalytic combustion) have inherent disadvantages. Adsorption requires periodic regeneration of the adsorbent. Incineration and catalytic combustion require high temperatures (150 °C–500 °C, depending on the catalyst and pollutants), and thermal methods do not remove metals [5]. Biological methods of air purification, based upon the ability of certain bacteria to degrade toxic organic compounds to produce carbon dioxide and water, may be considered an alternative to the traditional methods [6]. The ability of many microorganisms to adsorb metals onto their cell surface has also been observed [7]. These metals become a permanent part of the cell structure and are, therefore, not desorbed to rerelease the metal pollutant. The metals accumulate in the cell biomass and require periodic harvesting of the biomass for removal [7]. The removed metal-laden biomass can be treated for recovery of the metal.

Preliminary experiments using polymer fibers as supports for bacterial cell immobilization in the trickle-bed bioreactor show removal efficiencies ranging from 70% to 100% for various pollutants

(toluene, ethyl acetate, undecane, styrene, ethanol, etc.). The substrate concentrations varied from 10 to 300 mg/m<sup>3</sup> and the space velocity of air from 2500 to 20,000 hr<sup>-1</sup>. In other experiments, microorganisms were shown to accumulate metals in cell mass at concentrations 1000-fold above the water concentration. Total amounts of metal accounted for 1%-2% of the dry cell mass [7,8]. It is suspected that similar results will be possible in contaminated airstreams.

An estimation of the cost of these and other control technologies are needed as control strategies are developed. The EPA in its recent Mercury Study Report to Congress presented cost estimates for a variety of technologies. However, a more detailed economic analyses, with special emphasis on cost-sensitivity analysis, will help determine critical parameters to be evaluated in full-scale test burns, help direct research activities, allow the benefits of co-control to be evaluated, and allow potential cost reductions resulting from technology improvements to be evaluated.

### *Approach*

This project comprises three discrete tasks. The first task focuses on the use of hydrothermal treatment as thermal washing of contaminated waste and fossil fuels to remove associated trace elements from the solid material. The second task examines the use of **biofilters** for the removal of volatile metals and **organics from** stacks. The third task compares the cost-effectiveness of these and other HAP prevention and control technologies. The specific objective of the Environmental Aspects of Hydrothermal Treatment task is to determine the amount of toxic metals and chlorine that can be removed from a variety of high-volume waste streams using sub- and supercritical water. Bench-scale extractions are being performed using a multigram apparatus capable of thermally treating up to 20 g of solid material at temperatures and pressures both above and below the critical conditions of water. Experiments consist of loading approximately 10 g into the tubing reactor, preheating the furnaces to selected conditions, and flowing water through the fixed bed for a set period of time. Extractions are at 250°C and 800 psi (subcritical), 400°C and 2100 psi (steam conditions), and 400°C and 3300 psi (supercritical conditions) for each waste or solid fuel. Water/steam flows through the solids for approximately 30 min at the specified conditions prior to **depressurization** and sample collection. From the extractions, the solid residual is analyzed to determine how much mercury, cadmium, lead, and chlorine were extracted from the solid to the aqueous phase. Water and gas samples from those tests showing good mercury removal are also analyzed.

Metal and VOC (volatile organic compound) Removal from Gas Streams by Novel Filter-Based Trickle-Bed Bioreactors focuses on proof of concept, rather than process optimization, to investigate the capabilities of bioreactors to remove mercury and VOCs from airstreams. As part of this, the quantities of Hg<sup>2+</sup> and Hg<sup>0</sup> that the microorganisms can take up per unit cell mass and the breakthrough time of mercury through the bioreactor filters are being determined for use in preliminary full-scale reactor design. The test sequence begins with incubating the microorganisms and inoculating them on the **biofilter**. Once the filters have been impregnated with the biomass, the

filters are placed in the trickle-bed bioreactor. Three filters in series will be used to facilitate the collection of design information. The filters will be exposed to humidified air spiked with  $\text{Hg}^0$  and  $\text{HgCl}_2$ , a selected VOC, and  $\text{HCl}$ . The biomass is not sensitive to the other normal flue gas constituents [9]; therefore, to decrease the cost and complexity of the experiments, these will not be added to the synthetic gas mixture. The concentrations of trace metals and VOCs leaving the reactor will be measured to determine the effectiveness of the treatment method. Each of the biofilters will be digested and analyzed upon completion of each individual test to provide input for a mass balance. The experimental test matrix is designed to allow determination of the total amount of metals that can be adsorbed by the biomass and of the time-dependent removal of metals using the biofilters.

The goal of the economic analysis is to compare cost and effectiveness of various metal emission prevention and control technologies that are currently being researched or used commercially. Mercury control methods are the focus of the study. The approach has been to build models that are based on the major equipment costs. Fixed percentages of the equipment costs are used to calculate the other components of capital cost. Operating costs include raw materials and additional labor that are required due to the control technology. The review is utilizing available information in the literature, including process layouts, capital and operating costs, and level of control. Vendors and users are being contacted to get a generic technology description, costs, and levels of control. The cost for the two technologies being investigated in Tasks 1 and 2 and other EERC-developed technologies will be estimated by comparing them to existing technologies where data exist and/or by pricing major components to determine critical parameters. Sensitivity analyses are being performed to determine the impact of varying critical process parameters. The technologies being reviewed include conventional and advanced physical cleaning, hydrothermal treatment, activated carbon injection, fixed-bed adsorbers, flue gas condensers, and wet and dry scrubbing. A technology summary will be prepared for each control method evaluated, and the technologies will be compared in clear, concise tables and graphs.

### ***Progress***

The use of hydrothermal treatment for removal of mercury and other HAPs has been the focus of one of the major tasks under the CATM Year 5 program. To date, small batch experiments have been carried out on two sewage sludges (high and low levels of chlorine), RDF, petroleum coke, and raw crude oil. Additional work has been performed on two Illinois Basin coals under the CATM JSRP with ICCI. In addition, oxidizing agents, including acetic acid, formic acid, and hydrogen peroxide, have been used for several tests.

Available results show that almost complete removal of both chlorine (>99.9%) and mercury (89.6%–99.4%) can be accomplished with the sewage sludges. Results from the hydrothermal treatment of the high-chlorine sewage sludge are shown in the following table. Essentially all of the

### Results from Hydrothermal Treatment of Sewage Sludge

Temperature, °C	Pressure, psi	Species	Removed from Solid, %	Recovery in Condensed Phase <sup>1</sup> %	Recovery in Gas Phase or Reacted, %
250	800	Hg	89.6	3 ;	63
250	<b>800</b>	Cl	99.7	92	8
400	2000	Hg	98.4	14	86
400	2000	Cl	99.6	81	19
400	3500	Hg	98.9	16	84
400	3500	Cl	99.1	58	42

<sup>1</sup> Combined aqueous and organic phase.

<sup>2</sup> Determined by difference. Includes quantities in gas phase, that reacted or adsorbed on the metal reactor walls, and measurement errors.

chlorine is removed for all processing conditions tested. Under subcritical conditions, most of the chlorine is transferred to the aqueous phase, while at supercritical conditions, almost half of the chlorine is either released in the gas phase or has reacted with the metal walls of the reactor. Additional work needs to be done to close the chlorine balance and to determine the extent of any corrosion that may occur at the supercritical conditions.

To accomplish high levels of mercury removal from the sewage sludge, supercritical temperature but subcritical pressure (steam) is required. In all three cases, a significant fraction of the mercury is released in the gas phase. A zeolite or carbon filter would be used in an integrated system to concentrate the mercury and remove it from the gas phase. Although no leaching tests have been performed, it is anticipated that this material would be suitable for disposal.

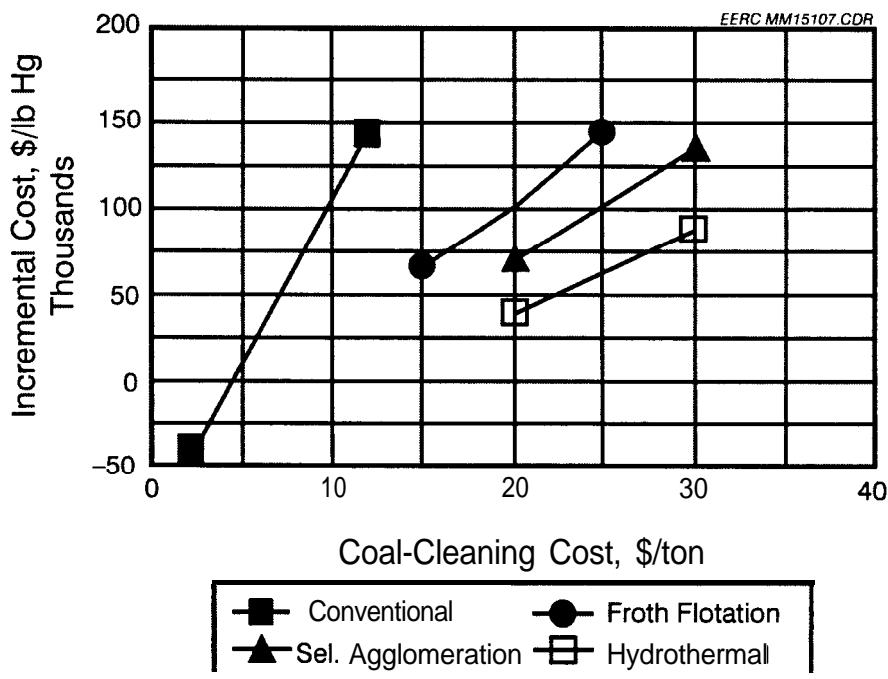
For the RDF case, the mercury appears to be bound rather tightly to the inorganic fraction and remains with the solid residue. Lead also follows this pattern. With the RDF, especially at the supercritical conditions, the organic fraction can be separated from the residual solids and could potentially be used as a clean-burning liquid fuel. It is speculated that the chlorine will remain in the water phase; therefore, the dioxin issue will be resolved in addition to the trace metals through hydrothermal treatment. For the RDF, since the mercury and other HAPs appear to be stable in the solid fraction even under the most stringent treatment conditions, the hydrothermal treatment of RDF may generate a solid material that can be safely disposed.

Extractions were performed with petroleum coke and crude oils. The premise behind the choice of these materials was that the hydrothermal processing conditions could potentially open the porphyrin groups that are the typical sites for vanadium, nickel, and other metals such as mercury. If these metals could be released from the porphyrins, then they could be extracted from the organic residue. Preliminary results, however, showed that hydrothermal processing, even at supercritical conditions, was not sufficient to remove any of the metals from the petroleum coke. These samples were further treated with  $\text{H}_2\text{O}_2$ , acetic acid, and formic acid, in the hope that these oxidizing agents would attack the sites binding the metals and provide a mechanism to release them from the organic matrix. No significant improvement was noted in metal reduction. The tests with the crude oils were equally unsuccessful in removal of nickel and vanadium from the organic matrix.

Work performed under a jointly sponsored project by CATM, DOE, and ICCI showed that both sulfur and mercury can be reduced from bituminous coals. Compliant coal was produced on the bench scale from a 3.5% sulfur coal. In addition, the following reductions in HAPs were noted: 99% mercury, 85% arsenic, 29% selenium, and 53% chlorine. The upgraded product had a heating value of 14,475 Btu/lb. Solids recovery for the process was only 68%; however, the energy recovery was significantly higher at 93%.

Work on mercury removal through trickle-bed biofiltration focused primarily on reactor design and establishing a viable growth of microorganisms. The most difficult task, the design and construction of a functioning bench-scale trickle bed bioreactor, has been completed. The prototype is currently undergoing shakedown testing with few complications encountered. Construction of the remaining four bioreactors is under way based on the successful design and operation of the prototype. The first prototype reactor will be ready for mercury remediation trials in early February.

The focus of the economic evaluation has been primarily on the coal cleaning. The cost-effectiveness of conventional coal cleaning, froth floatation, selective agglomeration, and hydrothermal treatment have been preliminarily compared. The primary cost of coal cleaning incurred by the utility company is an incremental increase in the price of fuel. This can range from \$2 to over \$30 per ton of coal. Coal cleaning, however, also offers a number of benefits to the utility in the form of lower  $\text{SO}_2$  emissions, lower operating and maintenance costs resulting from reduced ash content, and lower waste disposal costs. In analyzing the cost of mercury reduction using coal-cleaning methods, credits were given to offset these benefits. Based on the conservative estimates of \$1 00/ton  $\text{SO}_2$  reduced and \$20/ton for waste disposal, the incremental cost of using cleaned coal for mercury control was estimated, with results shown in the figure above. The mercury removal costs are shown as a function over the typical range of coal-cleaning costs for each of the technologies considered. The calculations are based on mercury removals of 21% for conventional cleaning, 55% for froth floatation, 68% for selective agglomeration, and 90% for hydrothermal treatment. The results show that conventional coal cleaning is very cost-effective, based on a \$/lb mercury removed. However, since conventional cleaning is only effective at removing low levels of mercury, it probably is not



*Cost of Mercury Control for Various Coal-Cleaning Methods.*

a viable method for mercury control. Of the advanced coal-cleaning methods, hydrothermal treatment shows the most promise, both in terms of achievable mercury levels and in cost. Mercury removal levels of 90% and greater have been demonstrated with Illinois Basin coal, with the incremental cost of mercury removal ranging from \$40,000 to \$84,000/lb Hg removed. This is within the range of costs of \$4920 to \$70,000/lb Hg removed presented by EPA in its recent report to Congress as the projected cost of mercury control in utility applications. Future work at the EERC will focus on optimizing the hydrothermal treatment process and developing more accurate cost estimates.

### *Status*

The experimental work for the hydrothermal treatment task is essentially complete for those samples currently on hand at the EERC. Additional analytical work and data interpretation are required to complete this work. The EERC is currently seeking a source of harbor dredging sludge for hydrothermal testing. The work with the biofilters is approximately half done. The filter media has been inoculated with microorganisms, and their growth on the filter is being established. These biofilters will be exposed to a gas stream containing various levels and species of mercury early in 1998 to determine their potential total uptake and rate of adsorption of mercury. Work will continue with the economic modeling, with attention focusing on improving sensitivity analysis already

performed for activated carbon injection and developing models for carbon bed filters, hydrothermal treatment, and biofiltration.

### ***Potential Users/Technology Transfer***

The hydrothermal treatment process has a wide range of applications, including preparation of premium-grade fuels, pollution prevention in waste incinerators, treatment of contaminated soils, and processing spent sorbents. The focus of the work on biofilters is directed mainly at providing pollution prevention options for small- and medium-sized businesses and has broad applications in industries such as metal fabrication and welding, steel foundries, smelting operations, some chemical processes such as chlorine production, fiberglass formulation, and others. The economic evaluation is focused primarily at the utility industry and should provide a valuable tool for use in evaluating mercury control options. Therefore, the benefits of this project will include, but extend beyond, the utility industry.

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## **DEVELOPMENT AND DEMONSTRATION OF TRACE METALS DATABASE**

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### ***Project Description***

The enormous amount of data generated in response to the increased awareness and concern regarding trace element transformation, analysis, and control is of marginal use if it is not easily accessible. To address the need for a more convenient and efficient method to utilize this ever-growing pool of data, a relational database and associated user interface were developed (Program Area 4). Information currently in the database was derived from compiled reports and test results from a variety of commercial, federal, and academic sources, including data derived from the ongoing CATM technical projects pertaining to trace element transformation, analysis, and control (Program Areas 1-3). The database has been demonstrated at various conferences and expositions and is also promoted during the Trace Elements Short Course (Program Area 5) as a tool to predict trace element emissions from fuel conversion and emission control systems.

### ***Goal***

Goals associated with this project are directed toward the development, maintenance, and improvement of tools used in the decision-making process involved in management, operation, and long-term planning of issues related to air toxic metals. Specific goals set and met in this year are as follows:

- Collection and critical review of new data
- Enhancement and debugging of the graphical user interface (GUI)
- Initial development and integration of a GIS with the CATM database
- Presentation of the use and capabilities of the CATM database at a national convention focusing on issues of air toxic metals

### ***Rationale***

The CATM database has been established to facilitate research on the prevention, transformation, behavior, and control of toxic metal emissions from energy-producing and incineration systems. The primary applications of the database are to aid in the development of methods to predict the fate of metals in fossil fuel systems, determine the effectiveness of control

devices, assist in identifying new control technologies, and provide source-emission data that can be used to assess health risks. The database provides an interactive user application from which users can quickly and efficiently access and display information relevant to their particular need or area of concern. The data are maintained in a relational database engine at the EERC; however, the application has been designed such that the data are accessible through the Internet.

### ***Approach***

The CATM database was developed to serve as a centralized storage media for air toxic metals data, accessible internally through the local area network and externally through the Internet. The information in the database is organized in three major categories: analytical, engineering, and materials. The database uses a samples-based approach; i.e., a sample must contain analytical information to be included in the database. Engineering information in and of itself is not included in the database, but is entered only in association with sample information. This approach was used so that the database remains focused on trace element emissions, as there are other databases containing strictly engineering or strictly analytical information. The CATM database links this information together, such that queries regarding samples can be related to engineering and/or analytical information along with geographical information coupled in a GIS system.

The application was designed so that navigating through the database is intuitive for the user. In addition, the intended users of the database—plant operators, researchers, government personnel, plant managers, *etc.*—were considered. Overall, the application was designed to be simple and user-friendly, yet provide a variety of data presentations to serve a specified variety of end users.

Here is an **example** of how the database may be applied in researching a specific topic:

**Question:** Since coal-cleaning processes commonly remove a substantial amount of pyrite, could we also expect removal of As and Hg?

**Approach:** Use the database to correlate the Fe concentration of a number of coals with their Hg and As contents. In addition, compare the As and Hg concentrations of pulverizer rejects produced during coal processing to the resulting feed coal (pulverizer rejects are commonly high in pyrite).

The ongoing collection and input of data are extremely important for the CATM database. Industrial participation will greatly benefit the database, as well as participation from other research organizations and government agencies. In dealing with new sources of data, especially industrial data, confidentiality and security features of the database are designed to satisfy the submitter of data. Security features are implemented as necessary to ensure the level of confidentiality requested by the submitter.

### *Progress*

The first version of the database application was completed in 1996. Data from nine full- and several bench- and pilot-scale systems were entered in the database. The bench- and pilot-scale data have been verified for input errors. Four more sets of system and analytical data have been added and are in the process of being verified for input errors. Data entry is an ongoing process that will continue throughout the CATM project.

Information in the database has been used to create an initial GIS system to display toxic metal emission data according to geographic location. The introduction of these data facilitates the usefulness and integration potential of the information contained in the CATM database. Readily available and consistent location identification data of permanent and full-scale facilities will support the development of environmental risk management strategies and assessments. The ability to link the geographical information within the CATM database with a commercially available GIS will be demonstrated.

The database was developed using client/server technology. Client/server technology allows for a physical separation between the residence of the data and the residence of the application. The data are stored in a database engine on a separate UNIX workstation that functions as a server. Traditional relational database management system design strategies were used to optimize data storage and retrieval. The application was created with **PowerBuilder** (PowerSoft, Inc.), a Windows-based, high-performance, object-oriented development tool. The application resides on users' individual computers and represents the client side of the architecture. The application presents the users with options for querying and displaying data through user-friendly forms and reports. Data are retrieved from the database through structured query language (SQL) calls to the server and displayed via the application on the user's PC. This arrangement takes advantage of the processing ability of the client's PC to perform functions such as sorting and arranging data that have been retrieved from the server. The server is optimized to interpret the SQL statements and perform database management functions.

The CATM application allows the user to develop very complex queries and provides many features for the display and manipulation of the retrieved data. To access the database through the Internet, a user must have access to an Internet provider and must be able to run a SLIP (serial line interface protocol) connection. (In most cases, if a user has an Internet provider, SLIP can be downloaded as freeware.) Once the SLIP connection is made, the user simply initiates the CATM application. This arrangement provides the users with all of the processing power of their PCs, i.e., speed. The only transfer of information over the Internet is the SQL statement sent to the server and the resulting data retrieved from the server and sent back to the clients' PCs. All of the other processing is executed on the individual PC. This is very important, as quick response time is essential for those using the database.

The Facility for Analysis of Chemical Thermodynamics (FACT) model has been acquired by the EERC to quantify chemical equilibria in various combustion and gasification systems. The FACT model is a comprehensive thermodynamic model that performs chemical equilibrium calculations for systems consisting of solid, liquid, gaseous, and/or aqueous phases. It contains a thermochemical database with more than 6500 species; 24 elements and 550 product species can participate in one equilibrium reaction; over 90 binary, ternary, and higher-order solutions are available to represent systems with **nonideal** mixing, such as slag and glass; FACT has the capability to model open systems (gas or liquids can be removed from the system in discrete intervals) to represent quasi-kinetic systems; options are available for systems to contain aqueous species, **nonideal** gases, and plasma ions.

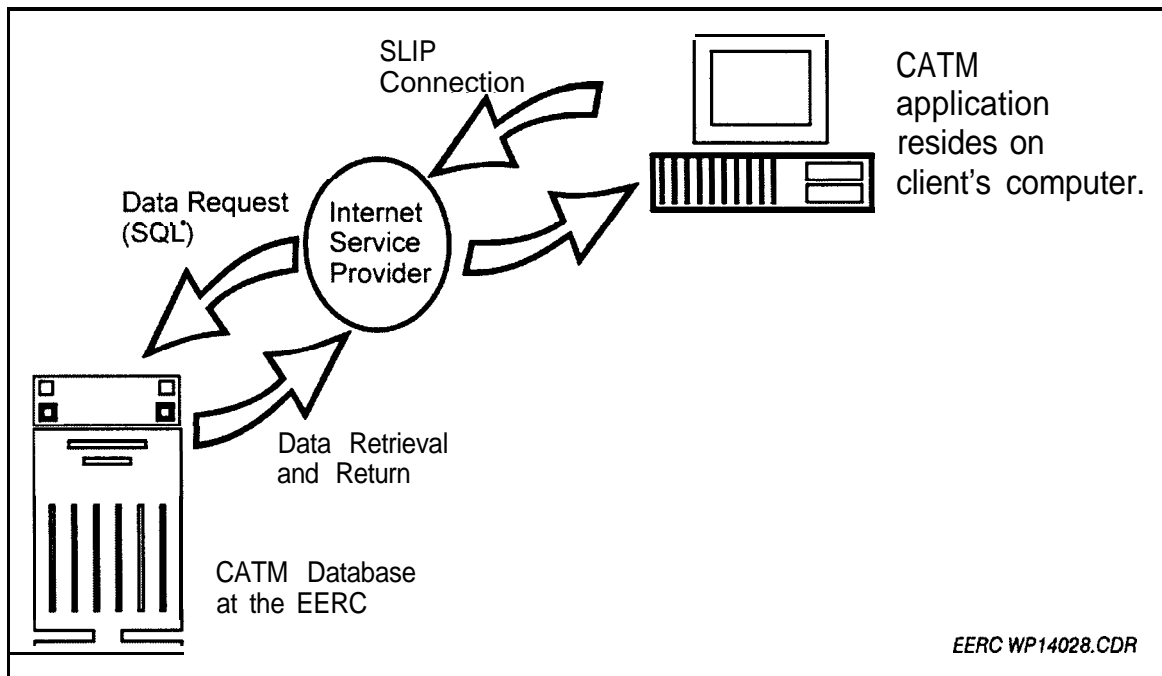
New or improved thermodynamic data can be easily added to the FACT database. The EERC has added over a dozen new compounds, mainly on trace elements. Optimized solutions have been added for a number of (nonstoichiometric) ash minerals. The FACT model contains graphical tools to display input data and results and to assist in the optimization of user-defined solutions. A special feature of the FACT code is the construction of phase diagrams that are helpful in identifying metastable equilibria. A composition can be graphed as a function of temperature, pressure, or compound concentration. Spreadsheet macros have been developed to link these output files and display the results in 2-D and 3-D graphs.

### ***Status***

The client application is now available either on diskettes or by being downloaded through the Internet via the World Wide Web. Intuitive screens and a variety of display and data manipulation options are available to ensure that the database is effective as a research and industrial tool. The focus for future work will be to enhance the options for displaying and graphing data, to add control technology efficiency models and cost of control economic data, and to modify the application in response to feedback from users.

### ***Potential Users/Technology Transfer***

The database has many practical applications, including investigating collection and removal efficiencies of control devices, comparing source emissions, comparing analytical results from **bench-** and full-scale operations, investigating the usefulness of various sorbents, comparing the size distribution of ash produced from a coal at varying run configurations, or comparing plant performance as a function of fuel type and quality.



*Architecture of Data Access Via the Internet*

## NICKEL SPECIATION OF RESIDUAL OIL ASH

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### *Project Description*

The speciation of Ni emitted from residual-oil-fired utility boilers requires investigation because the possible presence of small respirable particles containing nickel subsulfide ( $\text{Ni}_3\text{S}_2$ ) is a health concern. An experimental approach was used to investigate the Ni speciation of residual oil combustion ash. Ash from a low- and high-sulfur (0.33 and 1.80 wt%, respectively) residual oil was produced using a laboratory-scale combustion system at excess  $\text{O}_2$  concentrations of  $\leq 1$  and 2 or 3 mol%. Ni speciation analyses were performed using XAFS spectroscopy, sequential extraction-ASV, and CPEV.

### *Goal*

Research goals are threefold:

- Identify and quantify the chemical forms of Ni in No. 6 fuel oil combustion ash
- Investigate the effects of fuel sulfur (S) and excess  $\text{O}_2$  concentrations on Ni speciation
- Evaluate the comparability of Ni speciation analysis results obtained by sequential extraction-ASV, CPEV, and XAFS spectroscopy

### *Rationale*

Knowledge of the chemical speciation of Ni in the ash emitted from oil-fired boilers is important with regard to potential human exposure and adverse health effects. Specifically, the presence of small respirable particles containing  $\text{Ni}_3\text{S}_2$  is of primary concern from a human health standpoint. The chemical speciation of Ni emissions has been investigated recently using a modified EPA Method 5 sampling train in conjunction with a sequential extraction-ASV method. This method is based on treating a relatively small (10–100 mg) but representative ash sample to successive leaching steps to separate the analyte Ni species from the sample matrix. Ni in the extracted fractions is then analyzed using ASV, an electroanalytical technique. Ni speciation results from this method suggest that as much as ~25% of the total Ni emitted from oil-fired utility boilers occurs as a sulfide or subsulfide phase (e.g.,  $\text{NiS}_2$ ,  $\text{Ni}_3\text{S}_4$ ,  $\text{NiS}$ ,  $\text{Ni}_7\text{S}_6$ ,  $\text{Ni}_3\text{S}_2$ ) while the remaining 75% is apportioned among  $\text{NiO}$ , soluble Ni species (e.g.,  $\text{NiSO}_4$ ,  $\text{NiCl}_2$ , and  $\text{NiCO}_3$ ), nickel silicate(s), and elemental

nickel ( $\text{Ni}^0$ ). The capabilities of CPEV and XAFS spectroscopy to directly determine Ni speciation are being used to evaluate these sequential extraction-ASV speciation results. Although extraction methods determine speciation indirectly, they are necessary to make trace element speciation determinations more quantitative and readily available.

### *Approach*

Combustion tests were conducted using a CEPS, a 42-MJ/hr combustion system, to elucidate differences in the Ni speciation of ashes produced from low- and high-S fuel oils at excess  $\text{O}_2$  concentrations of  $\leq 1$  and 2 or 3 mol%. Detailed descriptions of the CEPS are provided in the CATM 1994-1995 Annual Report [1] and in a previous *CATM Newsletter* [2]. Bulk ash samples were collected at the inlet of the convection pass section of the CEPS using glass-fiber filters. The ash samples were analyzed first using XAFS spectroscopy because it is a nondestructive technique. Ni K-edge XAFS spectroscopy measurements were conducted on beam line X-19A of the National Synchrotron Light Source, Brookhaven National Laboratory, New York. XAFS spectra of reagent-grade Ni compounds were acquired and used essentially as “fingerprints” for identifying different Ni species. The five-step extraction procedure in the table below was also used for determining Ni speciation. Ni in each extract was quantified by ASV of nickel dimethylglyoxime collected on a hanging mercury drop electrode with a CH-620 electroanalytical system in square-wave voltammetry mode. Ni concentration was obtained by the method of standard additions. In addition to analyzing the Ni extraction fractions, total Ni was determined. Although this method currently cannot be used to discriminate between nickel sulfide and subsulfide species, CPEV was used to distinguish between  $\text{Ni}_3\text{S}_2$  and  $\text{NiS}$ . Mineral and synthetic standards of  $\text{Ni}_3\text{S}_2$  and  $\text{NiS}$  as well as ash and extraction residues were mixed with microcrystalline graphite powder and fashioned into CPEs. Cyclic voltammetry and linear sweep voltammetry were performed using a CH-620 electroanalyzer to identify  $\text{Ni}_3\text{S}_2$  and  $\text{NiS}$ .

**Five-Step Ni Species Extraction Procedure**

Extraction Steps	Ni Species
1M NaOAc–0.5M HOAc, pH 5, 25°C Bransonic bath	Soluble NiX (X = $\text{SO}_4$ , $\text{CO}_3$ , Cl,)
0.3M $\text{Na}_2\text{S}_2\text{O}_4$ –0.2M citrate, pH 5, 60°C, Bransonic bath	NiO
Electromagnetic	$\text{Ni}^0$
30% $\text{H}_2\text{O}_2$ –0.02M $\text{HNO}_3$ , pH 2, 85°C	$\text{NiS}_2$ , $\text{Ni}_3\text{S}_4$ , $\text{NiS}$ , $\text{Ni}_7\text{S}_6$ , $\text{Ni}_3\text{S}_2$
50% HF-aqua regia, microwave digest	Ni silicate(s)

### Progress

XAFS spectroscopy, sequential extraction-ASV, and CPEV measurements indicate that soluble  $\text{NiSO}_4$  and not the more toxic  $\text{Ni}_3\text{S}_2$  species predominate in low- and high-S residual oil ashes produced experimentally at excess  $\text{O}_2$  concentrations of  $\leq 1\%$  and 2 or 3 mol%. As indicated in the following table, the sequential extraction-ASV method detected the presence of significant proportions of  $\text{NiO}$  that was not detected using XAFS spectroscopy, even though the spectra of  $\text{NiO}$  are very distinctive from those for the dominant  $\text{NiSO}_4$  species. In future research, residue from the first step of the extraction procedure in the table on p. 44 will be analyzed using XAFS spectroscopy to corroborate the existence of  $\text{NiO}$  in residual oil ash. Fuel S content did not significantly affect Ni speciation; however, increasing excess  $\text{O}_2$  concentrations promoted Ni sulfation. The sequential extraction-ASV method also indicated the presence of very small proportions,  $<2\%$ , of nickel sulfide. Analyses of a high-sulfur oil ash sample and the extraction residues from this ash by CPEV suggest that the nickel sulfide is present as  $\text{NiS}$  and not  $\text{Ni}_3\text{S}_2$ . The proportions of sulfidic nickel ( $\text{Ni}_x\text{S}_y$ ) and  $\text{NiO}$  measured in these ash samples produced experimentally are much lower, while the relative proportions of soluble Ni are much greater than previous sequential extraction-ASV measurements of oil ashes collected from utility-scale boilers. Potential sources of these differences in Ni speciation include the sampling methods employed and the actual physicochemical properties of the ashes produced in a laboratory-scale versus utility-scale combustion system. Research is currently under way to identify the cause(s) of disagreement in Ni speciation results.

**Sequential Extraction-ASV Ni Speciation Analysis Results, %**

Ni Species	Low-S Oil		High-S Oil	
	$\leq 1\%$ Excess $\text{O}_2$	3% Excess $\text{O}_2$	$\leq 1\%$ Excess $\text{O}_2$	2% Excess $\text{O}_2$
Soluble Ni	78.7	89.8	74.2	92.3
$\text{NiO}$	16.6	5.4	23.5	6.1
$\text{Ni}^0$	0.5	0.2	0.3	0.1
$\text{Ni}_x\text{S}_y$	1.6	1.8	1.2	0.9
Ni silicate(s)	2.6	2.8	0.8	0.6
Total Ni. wt%	3.33	3.75	8.84	7.55

### Status

Preliminary results of this ongoing project are being published in the Journal *Combustion and Science and Technology*. In addition, results have been presented at the Fifth International Congress on Toxic Combustion Byproducts, Dayton, Ohio, June 25-27, 1997; the Fourth Annual Meeting of the Center for Air Toxic Metals, Grand Forks, North Dakota, September 16 and 17, 1997; and the

Managing Hazardous Air Pollutants Fourth International Conference, Washington, DC, November 12-14, 1997. This ongoing project is supported by a consortium of Amerada Hess Corporation, American Petroleum Institute, EPRI, Empire State Electric Energy Research Corporation, FPL, Hawaiian Electric Company, and Public Service Electric and Gas Company.

***Potential Users/Technology Transfer***

Information on the concentrations and occurrences of Ni species in residual oil combustion ash is required by industry to devise and implement effective emission control strategies, should they become necessary, and by regulatory agencies to properly assess health risks from metal emissions.

***References***

1. Center for Air Toxic Metals Annual Report 1994– 1995. Annual report for U.S. EPA Grant No. CR 823 173-01; University of North Dakota Energy & Environmental Research Center, Grand Forks, ND, 1995, pp 19-20.
2. “Construction of New Intermediate-Scale Combustion Test Facility Nears Completion,” *CA TM Newsletter* **1995**, 2 (1).

## **ATMOSPHERIC DEPOSITION: AIR TOXICS AT LAKE SUPERIOR**

Dennis L. Laudal (EERC), Thomas Erickson (EERC), Bruce Folkedahl (EERC), John Pavlish (EERC)

### ***Project Description***

The EPA in conjunction with the states of Wisconsin, Minnesota, and Michigan has been conducting studies to determine the deposition of mercury into Lake Superior. It is expected that a comprehensive test program will be funded in 1998 which is designed to determine the fate of anthropogenic mercury in the Lake Superior region and then determine the effect of mercury emissions on aquatic systems. It is expected that the data and predictive modeling based on the data will help determine the effect these emissions have in the whole Lake Superior region. CATM will help to coordinate the activities, work with personnel from the University of Michigan, Academy of Natural Science, and TetraTech to determine the state of the art of receptor methodology for trace elements and atmospheric modeling, share and discuss past research results and appropriate measurement methods with the team, and integrate EERC's emission models with available atmospheric models. The project has three primary tasks. Task 1 is to review the current state of knowledge of atmospheric sampling and atmospheric deposition models. Task 2 is to coordinate the efforts of the CATM project with the Lake Superior studies. The final task will be to link the EERC emission models with the deposition models that will be developed from the Lake Superior project.

### ***Goal***

The goal of the project is to determine the current state of knowledge for atmospheric sampling and receptors, interactions, reactions of emissions, deposition mechanisms, and atmospheric deposition models and to apply this knowledge to studies that are expected to be conducted at Lake Superior. The main objectives are as follows:

- . Perform literature searches on the above listed issues
- Interact with the research team for the Lake Superior study and supply them with the results of the literature searches
- Interact with the EPA and others on potential enhancement of mercury modeling
- Demonstrate the EERC point-source emission model in conjunction with an atmospheric deposition model

### ***Rationale***

This project in conjunction with the Fate of Mercury in the Lake Superior Region is designed to address the needs, as stated by the Science Advisory Committee, in the area of anthropogenic

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sources of mercury and its deposition both locally and regionally. The overall goal of the Lake Superior project is to provide data and modeling information that will help answer the question, *How does a change in mercury emissions from a source change the concentration of mercury in fish in a given area?* To answer that question, the concentration, species, deposition, and transport of mercury and cycling within lakes must be either measured or accurately modeled. The CATM portion of this project will begin to relate modeling of point-source mercury emissions with the atmospheric mercury models that will be enhanced as part of the overall project. In addition, the point-source models should help in determining the speciation of mercury at the stack. Good mercury speciation data are very important for modeling local, regional, and global deposition of mercury.

### ***Approach***

The project is divided into three tasks: review of the current state of knowledge, coordination with Lake Superior studies, and demonstration of models. Although the CATM project is linked with the proposed project “Fate of Mercury in the Lake Superior Region,” all but Task 2 can continue even if the Lake Superior project is not funded. Each task is described below.

#### **Task 1 – Review of Current State of Knowledge**

This task is to determine the current state of knowledge for atmospheric sampling and receptors, interactions/reactions of emissions, deposition mechanisms, and atmospheric deposition models. These reviews are being conducted through literature searches and communication with academia, government, and industrial groups.

#### **Task 2 – Coordination with Lake Superior Studies**

This task is to ensure that the insight gained from Task 1 is used to aid the studies at Lake Superior. As part of this task, CATM is contributing to all planning and management decisions for the proposed Lake Superior studies, and once the project is funded, CATM will continue to be very active in all planning decisions. This task will also track all results from the work conducted, and the data will be included within the CATM database.

#### **Task 3 – Demonstration of Models**

Currently, several models are used by EPA and other organizations to predict the resultant deposition pattern of emissions from an industrial process. The Lake Superior project will provide data that will enhance the accuracy and usability of these models to predict the deposition of mercury. CATM will work very closely with the University of Michigan’s Air Quality Laboratory and the EPA to link the TraceTran point source model (used by CATM) to the deposition models.

***Progress***

Most of the work to date has been in Tasks 1 and 2. The literature review is an ongoing activity. A research plan for the project entitled “The Fate of Mercury in the Lake Superior Region” is currently being reviewed by several agencies, including EPA, DOE, EnviroCanada, and EPRI.

Regular discussions are conducted between CATM personnel and Dr. Gerald Keeler from the University of Michigan’s Air Quality Laboratory. Dr. Keeler will be the person primarily responsible for conducting modeling activities in the Lake Superior region. CATM has helped Dr. Keeler develop a geographical understanding of the region surrounding the Clay Boswell Power Plant. The Clay Boswell plant will be one of the power plants that will be sampled. Using this information, Dr. Keeler has developed preliminary locations for deposition sampling. In addition, literature reviews and discussions are ongoing to provide information on tracers which will provide a link between the deposition samples and emissions from the power plant. Although no decisions have been made as to what tracers would work best, several rare-earth compounds are being discussed as possibilities.

## **DEVELOPMENT OF SPECIATION AND SAMPLING TOOLS FOR MERCURY IN FLUE GAS**

Jeffrey S. Thompson (EERC), Richard L. Schulz (EERC)

### ***Project Description***

Work under this project focuses on the development of new or improved methods to measure various forms of mercury in flue gas. The effects of the particulate collection assembly and the probe design on mercury speciation have been reported and are significant. Consequently, a new probe design, which minimizes cool spots in the probe and particulate collection assembly, has been designed and is under testing. The collection and detection of mercury species using a cryogenic trap has been tested. The design and construction of a thermally controlled cryogenic trap is under way and will be followed by rigorous testing under flue gas conditions. The combination of these two efforts will improve the methods to speciate mercury in flue gas so that the effects of mercury speciation on collection efficiencies for both existing and new technologies will be possible.

### ***Goal***

The goal of this work is the development of an inexpensive, rapid, and reliable method for the sampling and determination of the primary chemical forms of mercury in flue gas streams produced by coal-fired utilities, gasification systems, and municipal waste incinerators. Specific project objectives are as follows:

- Design, construction, and testing of a sample probe and particulate collection assembly with accurate temperature control for field work
- Design, construction, and testing of a cryogenic trap and detection system for mercury speciation in flue gas

### ***Rationale***

Current methods for mercury sampling and speciation for mercury (EPA Method 29) suffer from sampling effects, such as particulate partitioning and solution chemistry, that alter the chemical forms of mercury prior to detection. The development of alternative technologies for mercury sampling and analysis will eliminate these problems. This will allow the accurate determination of the chemical forms of mercury in flue gas. This is important for the ongoing development of control technologies as well as emission, transport, fate, and health-related issues.

## *Approach*

### **Probe and Particulate Collection Assembly**

The correct speciation of mercury requires that the mercury being measured be transported to the measuring device without altering its chemistry or concentration. Two factors that affect the transport of mercury are probe temperatures and particulate loading. CATM research is aimed at combining state-of-the-art heat tracing with new advances in insulation and probe design to produce a probe that will have as small of a temperature gradient as possible and to incorporate a particulate separation device to reduce the effects caused by fly ash. These two measures will help ensure that the mercury measurements are accurate for both speciation and total mercury.

### **Cryogenic Trapping of Mercury for Speciation**

The collection and subsequent desorption of mercury, as both mercuric chloride and elemental mercury, have been accomplished by using a cryogenic trap. The separation from other flue gas components (SO<sub>2</sub>, NO<sub>x</sub>, CO<sub>2</sub>, etc.) will be attempted with the use of a thermally controlled cryogenic trap, currently under construction. The separation of the mercury species from the flue gas components is a big step toward the accurate analysis of mercury species because it eliminates the interferences that complicate methods for mercury detection. The separation of mercury species from each other and their detection will be accomplished with the use of conventional gas chromatography techniques and currently available detectors as necessary.

## *Progress*

### **Probe and Particulate Collection Assembly**

The sampling probe has been built and tested at the bench-scale level with good results. Full-scale testing has revealed some small problems maintaining the temperature at the very last thermocouple on the sampling probe; this is partially due to the transition from the probe to the filter acting as a heat sink and partially due to problems maintaining the proper spacing of the heat trace lines at this transition. A modified probe has been built and is now ready for testing. Work, on incorporating the particulate removal device into the probe design, is under way and will soon be tested.

### **Cryogenic Trapping of Mercury for Speciation**

The efficient trapping of mercury (elemental and mercuric chloride) has been accomplished with the use of a simple glass-packed trap. Initial tests were conducted using liquid nitrogen as a cooling source so that temperature was not a limiting factor. The detection of the mercury was

accomplished with an atomic fluorescence detector for which the sensitivity is such that on-line instant detection of mercury was possible at relevant flue gas concentrations. The mercuric chloride was converted thermally to elemental mercury prior to detection. Following these initial experiments, a thermally controlled cryogenic trap was designed for use in testing the effect of temperature on collection efficiency and separation from other flue gas components. Construction of this trap is under way, and testing will begin shortly. The design of this trap includes an injection valve such that a clean carrier gas (helium) can be used for the desorption process. This should improve the sensitivity for mercury detection by atomic fluorescence by a factor of 50 to 100. In addition, the trap is designed with liquid nitrogen cooling with a thermostatically controlled valve to allow the separation of other flue gas components during the collection process.

The testing of the trap will allow the temperature to be optimized for efficient collection of mercury species with maximum separation of other flue gas components. It is anticipated that the completed unit will be used for pilot-scale measurements of mercury species for verification of the method.

### ***Status***

It is anticipated that this project will be completed in June 1998. The use of the tools developed during this research will continue to be used for other projects. The dissemination of details regarding these tools will be dependent on the pursuit of patent protection.

### ***Potential Users/Technology Transfer***

The tools developed under this project will benefit researchers in the pursuit of emission measurements for mercury species, development of control technologies, and transport and fate issues related to mercury species in the atmosphere. This work will also lay the ground work for the development of a commercial sampling probe and transport system to be used with a continuous emission monitor for mercury species if so desired.

## WET SCRUBBER SYSTEM

Michael D. Mann (EERC), Donald L. Toman (EERC), Christopher J. Zygarlicke (EERC), Kevin C. Galbreath (EERC), Dean N. Evenstad (EERC)

### *Project Description*

One of the primary goals of CATM is establishing a fundamental understanding of the fate of air toxic metal emission generated by the combustion of coal or other alternative fuels and the development of emission control strategies. The EERC has constructed and currently uses the CEPS as a well-controlled system for researching the impacts of toxic metal species formation resulting from combustion. The addition of a wet scrubber to the CEPS will allow CATM to test the effect that a wet FGD system has on emission control and metal transformations with regard to key elements like mercury, chlorine, and fluorine. In addition, the availability of a wet scrubber system will allow novel methods aimed at enhancing mercury removal in a FGD system to be tested.

### *Goal*

The goal of the proposed project is to develop a further understanding of the potential to capture toxic trace metal species by wet-scrubbing the flue gas generated by the combustion of selected coals. Trace metal species resulting from the introduction of sorbent chemical reagent material for sulfur capture will also be evaluated. Specific objectives necessary to attain this goal include the following: 1) design a wet scrubber system for flue gas sulfur dioxide capture to incorporate into the overall emission control system for the CEPS; 2) procure, construct, and shake down the wet scrubber system components; and 3) conduct limited testing to identify and quantify the concentrations of trace metal species introduced and captured utilizing a wet scrubber system as part of an overall flue gas cleanup system.

### *Rationale*

A current critical issue regarding mercury control is the upstream mercury species, because conventional wet scrubbers are currently under consideration as a possible method for gaseous mercury emission control. Gas-liquid contact time, gas diffusivity, and interfacial surface area are the limiting factors. Factors to increase or decrease these effects are already well characterized for commercial systems. The potential exists for reduced capture if mercury concentrations are highly elevated because of recycling of streams within the process. However, little if any of the mercury in gaseous, elemental, insoluble form is captured, even in the presence of aggressive oxidizing agents. Field data from nine process configurations compiled through DOE's project Phase I Assessment of Toxic Emissions from Coal-Fired Power Plants showed emission factors for mercury as high as  $11 \text{ lb}/10^{12} \text{ Btu}$ , even for systems utilizing advanced wet scrubbers. Percent penetration for mercury

ranged from less than 25% to 50% for systems with wet scrubbers. Current information, based on using the latest mercury speciation methods to sample at several full-scale scrubbers, suggests that wet scrubbers effectively capture almost all of the soluble oxidized mercury (e.g.,  $\text{HgCl}_2$ ) and capture little if any of the elemental mercury. Therefore, if wet scrubbers are to be considered an effective control method, the mercury must be in oxidized form before it reaches the scrubber. Several research projects are currently under way outside of the EERC to convert all of the mercury to oxidized form to facilitate better mercury control with scrubbers. This demonstrates the need to understand and be able to predict the mercury transformations that occur in the upstream combustion system.

A related issue regarding the transformation of mercury in scrubber systems is, what happens to the oxidized mercury that is captured? Although oxidized mercury capture in scrubber system components may meet an immediate need for reduced air emissions, the critical question is whether another problem is created. The final fate of the mercury is not complete until the stability of mercury in disposed or used scrubber products has been determined. At present, it is not yet known whether the oxidized mercury is chemically or thermally stable in the disposed or reused scrubber products. Most of the oxidized mercury forms captured are volatile, especially mercuric chloride, and thus appear to be highly susceptible to mobilization into the environment through desorption into the atmosphere or leaching into surface or groundwater. Several modes of transfer into the environment could occur upon direct disposal during wastewater and sludge treatment before disposal or during processing of commercial scrubber by-products such as gypsum. The potential for growing concern may exist about the fate of mercury captured from coal-fired power plant stack emissions as wet scrubbers are discussed in terms of mercury capture. The final fate of mercury in the environment is an important question for any mercury control method. These issues must be resolved if mercury capture in wet scrubbers is to become a long-term solution.

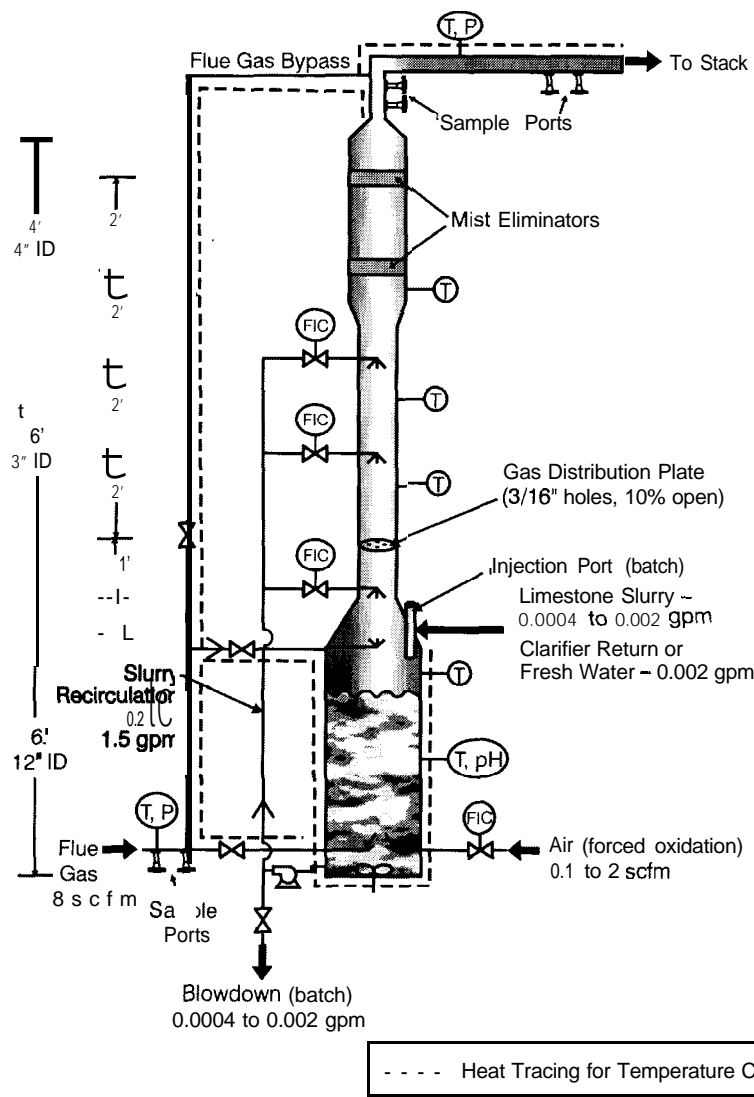
### ***Approach***

The current status of wet scrubber systems being used by the energy industry and utilities for burning coal or other alternative fuels was evaluated to allow design of an appropriate system. The system was selected, designed, and installed to allow representative chemical reactions to occur. Special consideration was given to the wall effects and other impacts related to the small size of the scrubber, and measures to counteract these effects were taken. The system was designed to be incorporated into the existing CEPS system.

### ***Progress***

A wet limestone scrubber has been designed for installation on the CEPS. During the design effort, careful consideration was given to methods to ensure that good gas-phase mass transfer would be obtained. A spray tower was chosen since it represents the most widely used FGD system. The proposed design consists of a 3-inch-diameter absorber tower with two stages (see figure below). A

narrow angle full-cone spray nozzle will be used to introduce the absorbing solution into each stage. The absorber tower sump will also serve as the absorber recirculation tank. This tank will be used to adjust the chemistry of the absorbent prior to circulating it through the tower and/or bubbling reactor. Control of the chemistry is also critical for simulating a full-scale scrubber, and provisions have been made to accommodate chemistry control in the absorber recirculation tank.



*Schematic of the EERC Subscale Wet Scrubber*

Therefore, a second mode of contacting is proposed. After flowing countercurrent to flue gas, the absorbent would drain into a second contacting vessel equipped with spargers similar to some of the advanced FGD units (Pure Air or Chiyoda) that utilize bubbling reactors rather than spray towers. The flue gas would be routed such that it could flow through the spargers to initiate contact with the absorbent in the bubbling reactor and then flow to the spray tower or to bypass the bubbling reactor and flow directly to the spray tower. The absorbent, likewise, would be piped so that it could pass through both the spray tower and the bubbling reactor or the bubbling reactor alone. This would allow operation of the spray tower and bubbling reactors either alone or in series. This allows both contacting methods to be investigated. In addition, should the spray tower prove to be inefficient at removing SO, because of poor mass transfer caused by wall effects in the absorber tower, the second bubbling reactor absorber can be used to ensure SO<sub>2</sub> levels comparable to industry could be obtained.

The wet scrubber is designed to operate over a fairly wide range of conditions. A gas velocity of 4 to 8 ft/sec should be achievable with the L/G ranging from 25 to 200 gal/1000 acfm. Either forced, natural or inhibited oxidation should be achievable. Other variables that can be controlled include chemistry (pH, [Ca], [Mg], [Cl], etc.), and flue gas injection temperature. The inlet gas concentrations can also be adjusted to investigate the impacts of a specific component on scrubber control through spiking of the CEPS flue gas.

### *Status*

The main scrubber system is installed and has been piped into the CEPS. Installation of monitoring and control instrumentation is in progress. Shakedown activities are planned for the first quarter of 1998.

### *Potential Users/Technology Transfer*

The CEPS with its mechanical collector, **baghouse** and wet scrubber provide a versatile tool for examining the fate of trace metals in a combustion system. The wet scrubber can be used to provide data to enhance the knowledge of metal capture in FGD systems. More importantly, methods to enhance mercury removal in FGD systems can be evaluated using tightly controlled experiments. Additionally, the fate of metals, once captured in the FGD, can be determined to evaluate the usefulness of the wet scrubber as a long-term viable solution for mercury control.

## **TECHNOLOGY COMMERCIALIZATION AND EDUCATION**

John H. Pavlish (EERC), Constance Y. Wixó (EERC), Cynthia M. Purfeerst (EERC), and Steven A. Benson (EERC)

### ***Goal***

The goal of Program Area 5 is to transfer technical information produced by CATM concerning trace metals to interested parties in research organizations and throughout the energy and environmental industry, as well as to provide training and educational opportunities for both students and professionals. Additionally, as products are developed and demonstrated through CATM, partnerships will be developed leading to commercialized technologies.

### ***Rationale***

Because of the time line that Congress has imposed on EPA, training, education, and dissemination of up-to-date information to industry and government agencies (EPA, DOE) in a timely manner are critical. Sharing and transferring the latest research findings to industry and EPA will greatly assist in establishing scientifically based regulatory standards.

### ***Approach***

In order to facilitate the sharing of information, several programs and meetings involving industry, government, research organizations, and the general public have been planned. In addition, educational institutes have been targeted to provide education on environmental issues, including pollution prevention and control technologies. Initially, efforts have focused on local education programs and on improving the curriculum at UND.

### ***Progress***

The fourth annual CATM meeting was held at the EERC in September 1997. The purpose of the meeting was to provide a forum by which industry, government, and the research community could exchange information on air toxic metals and provide direction for CATM's research, development, and commercialization programs. Approximately 60 people participated, representing the government (including EPA, DOE, MPCA, the Wisconsin Department of Natural Resources, USGS, and the Michigan Department of Environmental Quality), industry, and academic research organizations.

Highlights of the meeting included a presentation by Martha Keating of the EPA on the status of the "Mercury Report to Congress" and a panel discussion entitled "Mercury Regulations – What

Are the Options?" One of the major results of the discussion was the recognition that no cost-effective control technologies are currently available for utility applications to control elemental Hg.

The Science Advisory Committee (SAC) was restructured during the past year and is now one of two committees making up the Research Advisory Council (RAC). The other committee, the Partners Advisory Committee (PAC), has a representative from each of the current Affiliate members and a member from EPA. In December 1996, a draft Request for Ideas was sent to the PAC members for their input regarding research needs in the area of air toxic metals. Based on this input and input from other staff at the EERC, ten preproposals were mailed to the SAC in March 1997 for their technical review. Written comments and suggestions were returned to the CATM Director and Associate Director for preparation of the CATM 1997 program. A second meeting was held in conjunction with the fourth annual CATM meeting at the EERC in September 1997. At this meeting, the EPA Program Officer, PAC members, and CATM staff discussed CATM's future direction and identified and prioritized research needs. The EERC's newly hired Quality Assurance/Quality Control (QA/QC) Officer was also introduced and gave a short presentation on the direction of the QA/QC Program at the EERC and how it addresses CATM requirements.

The Affiliates Program has been well received and has generated significant interest by several sponsors. To date, EPRI, Otter Tail Power Company, Northern States Power Company (NSP), Tennessee Valley Authority (TVA), and the NDIC are official Affiliate Program members.

Part of the mission of CATM involves contributing to improved environmental education opportunities for students at UND. As a step toward that goal, CATM provided funding for UND faculty to develop stronger environmental education components in their courses. Two courses were selected for funding through a competitive review process. Dr. Theron Nelson of UND's Department of Finance is continuing the process of establishing an Environmental Issues minor for students throughout the College of Business and Public Administration (CBPA). Final approval by the CBPA's Curriculum Committee is pending. Dr. Douglas Ludlow of the UND Department of Chemical Engineering has incorporated pollution prevention and remediation issues into a **freshman**-level chemical engineering course. Both of these programs have or are expected to reach a large number of undergraduate students.

In September 1997, the EERC's volunteer Environmental Education Committee (EEC) teamed with the EERC's Red River Water Management Consortium (RRWMC), CATM, the city of Grand Forks, and additional volunteers to kick off the Storm Drain Stenciling Project. Storm drain stenciling is a simple and economical way to promote environmental education by teaching citizens that storm drains generally flow to the nearest river, lake, or stream without any treatment. Decreasing and eventually eliminating waste disposal directly or indirectly into storm drains is a way to prevent a major source of water pollution. The program consisted of volunteers using a 17- by 11 -inch stencil to paint a pollution prevention message next to street drains throughout the city: "DUMP NO

WASTE – DRAINS TO RIVER,” accompanied by the image of a fish. Volunteers also handed out informational flyers to the public that provide practical, easy-to-implement solutions to several stormwater pollution problems, such as disposal of motor oil, cleaning solvents, paint and paint thinner, gasoline, antifreeze, plastics, and yard waste.

Two issues of the *CATM* Newsletter were published and distributed to industry and other interested parties. The newsletter is circulated within all states of the United States and to over 40 countries internationally. The newsletter is designed to inform interested parties of air toxic issues and CATM activities and to encourage further participation and collaboration among industry and government. The newsletter is also available through the EERC’s home page on the World Wide Web at [www.eerc.und.nodak.edu](http://www.eerc.und.nodak.edu).

In February 1997, the EEC conducted its fourth annual waste audit. The audit involved taking inventory of 2 days’ worth of garbage generated at the EERC and sorting the waste into recyclable and nonrecyclable categories. The results were compared with the findings of the first three waste audits and showed that only 34% of EERC’s garbage is recyclable material, an all-time low in our waste audit history. This indicates that EERC employees are making good use of the recyclable collection bins placed throughout the work areas for white and mixed paper, cans, #1 and #2 plastic bottles, and glass. Total daily output continues to hover around half a pound per person for the third year in a row.

### **CATM Short Course**

A practical, 1-day short course on air toxic metals entitled “Trace Metals in Industrial Applications” was developed and presented to industry. The goal of the short course is to provide an overview of trace metal behavior and control in systems utilizing coal, oil, and natural gas or alternative fuels such as biomass, municipal solid waste, and RDFs. The course covers topic areas such as trace elements in fuels, sampling and analysis, trace element transformations and partitioning, control technologies, prediction and modeling, ash by-products, and a regulatory overview. The knowledge learned can assist in the design of new systems or the retrofit of existing units, can aid in the selection of coals and fuels for power generation, or can guide the blending of fuels to meet regulatory constraints.

The physical and chemical characteristics of all types of fuels are addressed in light of trace element content. The sampling and analysis sections cover the use of various standard and advanced techniques, the latest research in the development of methods, and the problems associated with determining trace element concentrations and emissions in power-generating facilities. Trace element transformations and partitioning during combustion and postcombustion processes are complex. This short course addresses the components involved, transformation types, and various approaches to studying transformations and partitioning. Control technologies, both conventional and advanced,

are addressed in relation to the latest DOE comprehensive report on HAPs. A section on predictive methods relates alternative methods to evaluate the fate and emission of trace elements in a given system and fuel type. Fuel conversion ash by-products of all types are addressed in relation to trace elements. The various types of ash material, the trace metal distribution, and methods of evaluating trace metal mobility of ash by-products are described. The regulatory section is an overview of the events leading up to and a discussion of the present regulatory situation.

### ***Status***

Ongoing activities will continue throughout the year. At present, at least two presentations of the short course are scheduled for 1998. The course is continually being upgraded to include new information from CATM projects and other research as it becomes available.

### ***Potential Users/Technology Transfer***

Program Area 5, Technology Commercialization and Education, will benefit industry and government agencies (specifically EPA and DOE) by providing information and data obtained from the CATM Program that will contribute to a much better understanding of air toxic issues and control of air toxic emissions. The general public will benefit through college courses that are environmentally sensitive and through numerous outreach programs initiated by CATM.

## ***RELATED PROJECTS***

**Mercury Formation and Fate** – Total funding: \$400,000. This project provides information that will assist in determining the potential impact of mercury emissions from North Dakota lignite-fired power plants on the bioavailability of mercury to humans. The specific objectives of this work conducted at the EERC are to determine the abundance and forms of mercury in flue gases emitted from lignite-fired power plants and to determine the source of mercury in Devils Lake, North Dakota. The first objective is focused on determining the forms of mercury emitted from North Dakota lignite-fired power plants, since the chemical form of mercury affects its transport through air, land, and water as well as its chemical and biological behavior. The second objective of the project will address discrepancies noted in the literature regarding the source of mercury in lakes. Some investigators indicate that the source of all Hg bioaccumulated in fish is from atmospheric deposition, while others indicate that much of the Hg is from natural sources or nonatmospheric anthropogenic sources. The degree of natural enrichment of mercury can be documented in the watersheds and sediments of various North American surface waters. These natural enrichment data can be used along with the potential for atmospheric deposition to assess the source of mercury in lakes. The major source of high levels of methylmercury that can be bioaccumulated in fish may not be from the atmospheric deposition of mercury derived from coal-fired power plants. This work will be coordinated with Dr. Jan Hulla of the University of North Dakota Pharmacology and Toxicology Department, who is proposing a project to determine the bioavailability of mercury in Devils Lake fish to humans.

**Strategic Studies** – Total funding: \$42,936. The overall goal of Strategic Studies, an ongoing task under the EERC-DOE Base Cooperative Agreement, is to understand the potentialities, limitations, and status of competing energy technologies in terms of scientific basis, state of development, technical barriers, cost, efficiency, policy treatment, and environmental performance. Products include white papers dealing with 1) energy policy, energy technologies, and related environmental technologies; 2) a review of energy and environmental issues for East Central Europe; and 3) focused review and analysis of U.S. environmental policy areas, including those addressing air emissions. The Strategic Studies task was initiated in 1989.

**Environmental Technology Systems Engineering and Cost Savings Analysis** – Total funding: \$1,150,000. To ensure the best allocation of resources for cleaning up the former U.S. defense sites, DOE has been aggressively using systems engineering and cost-savings analysis to aid in financial decisions. The EERC is working through WPI to provide the government with the expertise and resources to integrate systems engineering into its yearly process of budgeting and to perform cost analyses on existing and innovative technologies to be used in successful completion of the 200 (1 O-year) plan. This project was initiated in 1996 and is anticipated to continue for a minimum of 5 years.

**Evaluate the Fate and Distribution of Trace Elements in Integrated Gasification Systems** – Total funding: \$1,250,520. The potential problems associated with trace elements for integrated gasification combined-cycle (IGCC) and integrated gasification fuel cell (IGFC) technologies are the release of elements considered air toxics into the environment and the degradation of fuel cell efficiency because of contamination with minor elements. The trace elements being studied in this project are Pb, Hg, Ni, Cr, As, Se, and Cd. The objectives are to identify and model important physical and chemical transformation mechanisms of the trace elements during gasification as a function of coal compositions (trace element abundance and association) and gasification conditions. Identification of the reactions and transformations coupled with the ability to accurately model trace element behavior will provide essential information for the identification of the form of the inorganic species. This information will be used to identify the most effective control technologies. Emphasis is placed on providing a model that will benefit industry's use of coal gasification processes. This project began in 1992 and is scheduled for completion in early 1998. The project is funded by DOE.

**Impacts of Agricultural Chemicals on Groundwater in the Northern Great Plains** – Total funding: \$154,124. The objective of this program is to provide a scientifically valid basis for management and regulation of agricultural chemicals by developing an understanding of their occurrence, transport, and fate in representative settings in the northern Great Plains. In 1996, the scope of the program was expanded to include additional water management issues in the Red River of the North Basin under the RRWMC. A major objective of the RRWMC is to use results from the initial phases of this research program to find economical, practical, and timely technical solutions to regional water problems. Nonpoint-source pollution from agricultural and urban sources can cause the degradation of groundwater and surface water. Project field sites vary as to geology, hydrology, climatic conditions, crops grown, and farm management practices. Several specific factors being investigated include the effects of irrigation on the potential for groundwater contamination by agricultural chemicals, the role of preferential flow mechanisms on pesticide transport and fate, and the function of wetlands in agricultural settings. Additional laboratory studies include the determination of effects of soil characteristics on pesticide transport, the role of denitrification on aquifer nitrate occurrence and distribution, and the role of airborne particulates in pesticide transport. The USDA-funded project began in 1989 and is currently supported through 2001.

**Subcritical Water Extraction of Mercury from Soils and Sediments** – Total funding: \$40,000. The EPA's "National Sediment Quality Survey" lists the top pollutants responsible for toxicity in watersheds as 1) polychlorinated biphenyls (PCBs), 2) mercury, and 3) other organics such as polycyclic aromatic hydrocarbons (PAHs) and pesticides. In addition, these same pollutants are major contributors to chemical pollution on DOE and other contaminated sites (e.g., industrial sites, harbors). An ideal remediation method would allow cost-effective removal of both organic and mercury contamination using a single process. The EERC has previously shown that hazardous organic pollutants such as pesticides, PAHs, and PCBs can be completely removed from soils, sludges, and sediments at temperatures (250°C) and pressures (<50 atm) that are much milder than

typically used for supercritical water processes (temperature  $>374^{\circ}\text{C}$ , pressure  $>22.1\text{ atm}$ ). The present project demonstrated that subcritical water extraction can be used to remove mercury from highly contaminated soils using the same conditions ( $250^{\circ}\text{C}$  to  $300^{\circ}\text{C}$ ) which are effective to remove common organic pollutants such as PCBs and PAHs (e.g., coal tar), demonstrating that subcritical water extraction may be a useful approach for the remediation of materials cocontaminated with mercury and organic pollutants. The project was funded by DOE.

**Formal Evaluation of Chemical Measurement Methods: Mercury Speciation Measurements in Coal Combustion Systems** – Total funding: \$3,111,335. The 1990 Clean Air Act Amendments (CAAA) require the U.S. EPA to assess the health risks associated with Hg. It appears that the rate of Hg deposition and the type of control strategies used may depend on the type of Hg emitted. For the past 3 years in a project sponsored by EPRI and DOE, the EERC has been evaluating different mercury speciation methods at the bench and pilot scale. Four impinger-based methods and a dry sorbent method have been tested at the EERC: EPA Method 29 and three modifications of this method—the Ontario Hydro method, the tris-buffer method, and a method proposed by Research Triangle Institute (RTI); the dry sorbent method is the Mercury Speciation Adsorption method (MESA) developed by Frontier Geosciences. Each of these methods has advantages and disadvantages. The bench- and pilot-scale data show that, under certain conditions, EPA Method 29 and the MESA method do not appear to speciate Hg correctly. The tris-buffer and Ontario Hydro methods have been shown to have the most potential for success, and tests are under way to verify these methods as valid Hg speciation methods in a pilot-scale coal-fired system. This project was initiated in 1994 and is scheduled for completion in 1997.

**Hot-Gas Filter Cleanup and Testing of Trace Elements** – Total funding: \$2,672,813. The objective of the hot-gas cleanup (HGC) work on the transport reactor demonstration unit (TRDU) is to demonstrate acceptable performance of hot-gas filter elements in a pilot-scale system prior to long-term demonstration tests. The primary focus of the experimental effort is the testing of hot-gas filter element performance—particulate collection efficiency, filter pressure differential, filter cleanability, and durability—as a function of temperature and filter face velocity during short-term operation (100 to 200 hours). The filter vessel is used in combination with the TRDU to evaluate the performance of selected hot-gas filter elements under gasification operating conditions. Secondary objectives of this work are to evaluate the performance of the transport reactor, including general operability, ash transport and deposition, and trace element distribution and emission. The work directly supports the power systems development facility (PSDF) utilizing the M.W. Kellogg transport reactor located in Wilsonville, Alabama, and indirectly, the Foster Wheeler advanced pressurized fluid-bed combustor also located at Wilsonville. The project began in December 1994 and is scheduled for completion in June 1998. The project is funded by DOE.

**Review and Assessment of Results from the Comprehensive Characterization of Air Toxic Emissions from Coal-Fired Power Plants** – Total funding: \$700,000. To help meet the requirements

of the 1990 CAAA, DOE sponsored Phase I of a study entitled “Comprehensive Characterization of Air Toxic Emissions from Coal-Fired Power Plants.” The EERC served as an independent third-party reviewer of field test reports from this study. The objective of the project is to provide an independent review of reports produced from the air toxic emissions study, evaluate the scientific validity of the conclusions, identify significant correlations between emissions and fuel or process parameters, compare the data with available results from EPRI studies, make recommendations for future studies, and complete a report that summarizes Phase I results. The Phase I summary report was completed in September 1996 and is available from DOE. Phase I of the project began in 1994 and was completed in 1996.

**Sorbent Development for Mercury Control** – Total funding: \$255,000. Sorbent development for Hg control is the subject of a strategic research initiative at the EERC. Mercury emission control standards have been established for incinerators, and Hg control requirements for coal-burning utilities are under consideration by EPA. Large unexplained variations in the amounts of Hg captured and retained in conventional particulate control devices and acid gas scrubbers, together with questions concerning the stability of the captured Hg after disposal, mean that existing technologies cannot provide reliable control now, and their future contribution is uncertain. Both metallic ( $\text{Hg}^0$ ) and oxidized ( $\text{Hg}^{2+}$ ) forms of Hg have appreciable vapor pressures throughout the combustion train and at stack gas temperature. Various carbon-based sorbents have been shown to effectively control Hg at temperatures below  $120^\circ\text{C}$ , but no commercial sorbent is available to reliably control metallic Hg emissions at air heater exit temperatures of  $135^\circ$  to  $175^\circ\text{C}$ . A recent breakthrough at the EERC has achieved high rates of adsorption for both  $\text{Hg}^0$  and  $\text{Hg}^{2+}$  at moderately elevated temperatures. However, designing effective control measures will require a thorough understanding of the physical and chemical adsorption mechanisms that operate over a range of temperatures from  $95^\circ$  to  $315^\circ\text{C}$ . The objectives of the current research are to understand capture mechanisms for  $\text{Hg}^0$  and  $\text{HgCl}_2$  and to develop improved Hg sorbents for  $\text{Hg}^0$  and  $\text{HgCl}_2$ , based on the capture mechanisms. Newly developed and commercially available sorbents will be tested under conditions that are representative of the process ‘conditions of coal-fired combustors and incinerators. This project began in January 1997 and is scheduled for completion on June 30, 1998. The project is funded by DOE.

**Potential to Control Mercury from Coal-Fired Boilers by Using Sorbents** – Total funding: \$1,789,450. The primary goal is to determine the potential to control air toxic emissions in conventional particulate control devices. For volatile elements such as Hg, effective control may depend on the surface adsorption properties of the fly ash or added sorbents. Introduction of small amounts of high-surface-area materials, such as activated carbon, ahead of a particulate control device may provide effective Hg control. Parametric pilot tests were conducted to evaluate independent variables such as sorbent type, sorbent concentration, temperature, and coal type. The pilot-scale results show that carbon sorbents can provide 90% Hg control under some conditions, but predicting the level of control has proven difficult. Therefore, the focus of the program has switched from pilot-to bench-scale tests to evaluate sorbents for Hg control and provide information used to model the

kinetics of the uptake of Hg by sorbents. To date, the Hg capture ability of activated carbon sorbents has been evaluated at a number of different test conditions. The project began in 1993 and will be completed in 1998. The project is funded by DOE and EPRI. The draft final project report is being reviewed by EPRI and DOE. The final version of the report is planned for completion by April 1, 1998.

**Advanced Hybrid Particulate Collector, A New Concept for Air Toxics and Fine-Particle Control** – Total funding: \$1,495,646. A new concept in fine particulate control, AHPC, is being developed at the EERC under funding from DOE. The AHPC uniquely employs electrostatics and filtration in the same compartment providing major synergism between the collection mechanisms, both in the particulate collection step and in transfer of dust to the hopper. By effective utilization of these collection mechanisms, the AHPC is able to achieve very high collection efficiency of fine particles with much less collection area than conventional electrostatic precipitators (ESPs) or fabric filters. Ultrahigh fine-particle collection is achieved by removing over 90% of the dust before it reaches the fabric and using a GORE-TEX® membrane fabric to collect the particles that reach the filtration surface.

In Phase I of the development testing of the AHPC on a coal-fired combustor, particulate collection efficiencies greater than 99.999% for all particle sizes from 0.01 to 50  $\mu\text{m}$  were achieved, and trace emissions of arsenic, cadmium, lead, and nickel were below detection limits. Mercury and selenium were detected in measurable quantities in vapor form at the outlet, but were significantly reduced when a sorbent was injected upstream of the device. Method 29 data indicate collection efficiencies at least in the range from 99% to 99.9% for the nonvolatile trace elements, but the detection limits with Method 29 do not allow accurate measurement beyond about 99.9%. The fine-particle efficiency data indicate the actual collection efficiency for particulate trace elements is significantly higher. The AHPC offers a new approach to meet the challenge of collecting PM<sub>10</sub> and air toxic trace elements with an ultrahigh efficiency. In Phase II, plans are to scale up the AHPC to the 9000-acfm size and test on a slipstream at a power plant.

**Mercury Capture and Speciation on Solid Surfaces, Aerosols, and Wet Scrubber Solutions** – Total funding: \$160,000. The generation of laboratory data required to understand Hg capture and emission mechanisms associated with coal-fired boilers was the primary goal of this project. This information is directly used in the development of Hg sampling, analytical, and control methods at the EERC. Project subtasks included an assessment of fly ash Hg capture related to chemical and physical ash properties, a determination of Hg associations with submicron aerosols, evaluation of Hg capture on metal sorbents, and an investigation of the effect of wet scrubber solution chemistry on Hg speciation in flue gas. The project began in 1996 and was completed in December 1997. The project was funded by DOE.

Results from the **subtask** to evaluate sorption of elemental mercury by coal combustion fly ash showed that there appears to be a direct correlation between carbon content and mercury partitioning among individual ash samples. Also, there is a direct relationship between carbon content and mercury-sorbing capacity, although it is not directly correlated with the amount of carbon between the separated carbon fractions. Results from the activity to determine Hg associations with submicron aerosols showed that none of the four aerosols tested (KCl, SO<sub>3</sub>, NaNO<sub>3</sub>, and NaSO<sub>4</sub>) captured a significant amount of elemental mercury. All except NaNO<sub>3</sub> showed significant mercuric chloride removal. The KCl aerosol showed the highest mercuric chloride removal (87%), and the percentage removed was independent of the KCl concentration. Results from the **subtask** to evaluate elemental Hg removal from a nitrogen gas stream using metal sorbents showed that neither zinc nor tin, in reagent-grade metallic form, effectively captures elemental mercury. However, gold-coated silica sand (with Au loadings of 0.125%, 0.250%, and 1.000% by mass) was very effective at removing elemental mercury even with short residence times (0.03 sec) in the filter bed.

**Mercury Vapor Flux Measurements** – Total funding: \$27,571. The EERC has been contracted by PTI Environmental Services to conduct active and passive mercury flux measurements from soils at an industrial site in New Jersey. The active flux chamber available at the EERC is an adaptation of the U.S. EPA isolation flux chamber that is used to measure volatile emissions from solid and liquid surfaces. The resulting determination of mercury concentration in the air provides the client with baseline information used in site assessment and risk analysis.

**Fate and Transport of Trace Elements in Groundwater** – Total funding: \$800,000. Addressing concerns of gas industry personnel and regulators about Hg releases at metering sites, this project is designed to define the occurrence, transport, and fate of Hg in air, water, and soil at natural gas production sites that had been instrumented with Hg-based gas flowmeters in the past. The primary focus was initially on determining the potential for Hg contamination in groundwater at these sites. The scope was later broadened to include determinations of the spatial distribution of Hg in soil. Air concentrations were determined as a health and safety routine. Six field research sites located in three natural gas production areas of the United States (Louisiana, New Mexico, and Pennsylvania) were investigated with the intent of determining any adverse impact of inadvertent Hg releases on vulnerable environmental media in the vicinity of gas Hg manometer flowmeters. Results indicate that at the study sites, the transport of Hg from a surface release appears to be extremely limited, with no apparent adverse impact to shallow groundwater and air and a spatially limited impact to soils and sediments in the immediate vicinity of the flowmeters. The project began in 1992 and was completed in 1996. The project was funded by DOE and GRI.

**Recovery of Mercury from Contaminated Primary and Secondary Liquid Wastes** – Total funding: \$294,192. Mercury contamination in aqueous streams has long been identified as a hazard to human health and the environment. The EERC has teamed with ADA Technologies Inc., a small business located in Englewood, Colorado, to demonstrate a mercury removal and recovery process

for the remediation of primary and secondary liquid wastes. The process is based on the selective removal of mercury using noble metal sorbents developed by ADA. The sorbent can then be thermally regenerated to recover the mercury and reuse the sorbent. The EERC developed preliminary engineering data at the bench scale, designed and fabricated a 30-L/hr prototype test unit with integrated sorption and regeneration capabilities and, in conjunction with ADA and Oak Ridge National Laboratory, is currently evaluating system performance in the field at the Y-12 plant in Oak Ridge, Tennessee. The project, which is funded by DOE, began in January 1997, and the field trials are anticipated to run through September 1998.

**Environmental Management Technology Demonstration and Commercialization** - Total funding: \$4,380,407. At numerous locations across the nation, DOE is facing the monumental task of cleaning up environmental contamination at nuclear weapons facilities and other sites, a process that has been estimated to take 30 years and cost hundreds of billions of dollars. The EERC is an active partner in DOE's Environmental Restoration and Waste Management Program, which is aimed at demonstrating and commercializing new technologies to characterize and clean up these sites. The EERC's Environmental Management (EM) Program is working to commercialize new cleanup technologies in two ways: 1) through research, development, and demonstration of our own technologies, leading to partnerships with the private sector in commercialization and 2) by providing the private sector (especially small businesses) with the expertise and technical resources needed to take their technologies to the marketplace. This project began in 1994, with an initial duration of **5 years**.

**KEY PERSONNEL**

<b>Department/Section</b>	<b>Name</b>	<b>Title</b>
Environmental Protection Agency	William G. Stelz	Environmental Scientist <b>EPA</b> Program Officer
Energy & Environmental Research Center	Steven A. Benson	Associate Director for Research <b>CATM</b> Director
	John H. Pavlish	Senior Research Manager <b>CATM</b> Associate Director
	Gerald H. Groenewold	EERC Director
	Michael L. Jones	Associate Director, Industrial Relations and Technology Commercialization
	Edward N. Steadman	Associate Director for Research
	Everett A. Sondreal	Principal Research Advisor
	Thomas A. Erickson	Senior Research Manager
	Michael D. Mann	Senior Research Manager
	Stanley J. Miller	Senior Research Manager
	Karen A. Katrinak	Manager, Natural Materials Analytical Research Laboratory
	Christopher J. Zygarlicke	Research Manager
	Dennis L. Laudal	Research Manager
	Bruce C. Folkedahl	Research Scientist
	Grant L. Schelkoph	Research Engineer
	Wesley D. Peck	Research Associate
	Donald O. Toman	Research Associate
	Vit Kühnel	Research Hydrogeologist
	Roy B. Beard	Manager, Computer Systems
	Paul R. Hanson	Student Research Technician
	Andrew B. Maki	Student Research Technician
	Jeffrey S. Thompson	Research Associate
	Richard L. Schulz	Manager, Particulate Research Laboratory

Continued . .

**KEY PERSONNEL**, continued

<b>Department/Section</b>	<b>Name</b>	<b>Title</b>
	Kevin C. Galbreath	Research Associate
	Carolyn M. Lillemoen	Manager, Analytical Research Laboratory
	Constance Y. Wixo	Administrative Manager
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	David J. Hassett	Senior Research Advisor
	Brian C. Young	Senior Research Advisor
	Edwin S. Olson	Senior Research Advisor
	Debra F. Pflughoeft-Hassett	Research Manager
	Chris M. Anderson	Research Manager
	Steven B. Hawthorne	Senior Research Manager
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	David W. Brekke	Research Manager
	Donald P. McCollor	Research Associate
	Ted R. Aulich	Research Associate
	Robert O. Ness, Jr.	Research Manager
	Grant L. Schelkoph	Research Engineer
	Jay R. Gunderson	Research Manager
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University of North Dakota Dept. Chemical Engineering	Douglas K. Ludlow	Associate Professor
University of North Dakota Dept. Finance	Theron R. Nelson	Professor and Chair
University of North Dakota Dept. Geology and Geological Engineering	Frank R. Kamer	Professor

**OTHER PARTICIPANTS**

<b>Institution/Company</b>	<b>Name</b>	<b>Title</b>
Electric Power Research Institute	Babu Nott Paul Chu Ramsey Chang Winston Chow  Barbara Toole-O'Neil	Manager, Toxics Monitoring Manager, Toxics Control Project Manager Team Manager, Pollution Prevention and Environmental Control Manager, PISCES Trace Emissions Database
Northern States Power Company	Todd Albertson Patti Leaf	Fuel Resources Engineer Environmental Scientist
<b>New</b> York State Electric and Gas Corporation	John Smigelski Mehdi Rahimi	Principal Engineer Senior Environmental Engineer/ Generation
Consolidated Edison/Empire State Electric Energy Research Corporation	Jack Pirkey	Principal Engineer
Florida Power & Light	Ed Zillioux	Environmental Toxicologist
Montana-Dakota Utilities Co.	Gary Gress	Power Production Manager
Minnesota Power Company	Timothy Hagley	Environmental Engineer
Basin Electric Power Cooperative	Robert Eriksen	Administrator for Environmental Compliance
Cooperative Power Association	Will Kaul  Russ Nelson	Director, Environmental and Regulatory Services Engineering Superintendent
University of Connecticut	Joe Helble	Professor
CSIRO, Australia	Dalway Swaine	CATM Program Advisor
Public Service Electric & Gas Company	Edward G. Waugh	Engineering Manager, Air Toxics
U.S. EPA Air and Energy National Risk Management Research Laboratory	William Linak	Research Scientist and Project Officer
Physical Sciences, Inc.	Constance Senior  Lawrence Bool	Manager, Chemical Process Development Principal Engineer

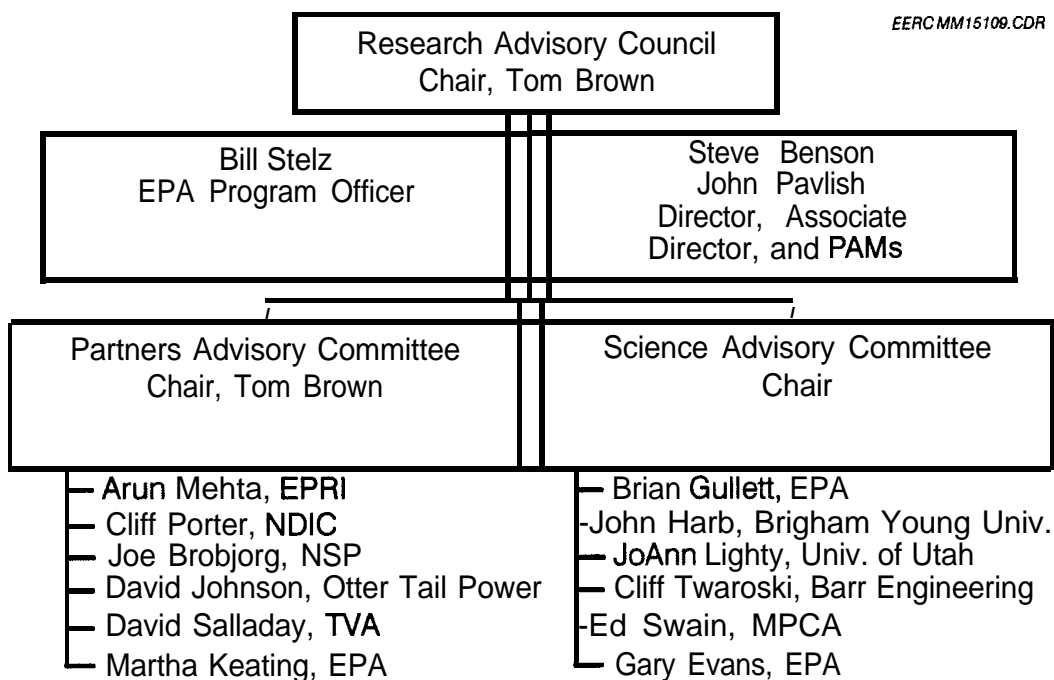
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**OTHER PARTICIPANTS**, continued

<b>Institution/Company</b>	<b>Name</b>	<b>Title</b>
Naval Air Warfare Center	Michael Seltzer	Research Chemist
American Board of Toxicology (ND)/ UND Dept. Pharmacology and Toxicology	Janis Hulla	Diplomate/Assistant Professor
Wisconsin Department of Natural Resources	Douglas Knauer	Chief, Environmental Contaminants
RMB Consulting & Research	Ralph Roberson	Principal
Reinhold Environmental Ltd.	Susan Reinhold	President
U.S. Department of Energy Federal Energy Technology Center-Pittsburgh	Charles Schmidt	Program Coordinator
Ontario Hydro	Blair Seckington William Dick  Leonard Terplak	Chief Advisor, Technology Senior Engineer, Business Program and Development Senior Engineer, Environment Dept Fossil Energy Unit
Minnesota Pollution Control Agency	Carol Andrews	Project Coordinator
United States Geological Survey	Allan Kolker	Geologist
ADA Technologies, Inc.	Richard Schlager	Senior Research Engineer
CONSOL, Inc.	Matt DeVito	Research Group Leader
U.S. Department of Commerce	Russ Bullock	Meteorologist
North Dakota Clean Water Action	Sherry Shadley	North Dakota Program Coordinator
University of Kentucky	Frank Huggins Gerald Huffman	Research Professor Director
Frontier Geosciences, Inc.	Eric Prestbo	Research Scientist

## ***RESEARCH ADVISORY COUNCIL CHARTER***

In response to comments provided by EPA's Peer Review Panel, the EERC, this year, proposed to change its existing CATM review committee structure to that shown below. The newly formed RAC consists of two committees, referred to as the PAC and the SAC. This committee structure should eliminate any perceived conflicts of interest expressed by the Peer Review panelists. In short, the role of the PAC will be to identify research needs and ideas, whereas the role of the SAC will be restricted to scientific review of proposed research activities. The structure of the RAC, PAC, and SAC is shown below.



PAM: Program Area Managers.

***Partners Advisory Committee***

<b>Member/Affiliation</b>	<b>Address</b>	<b>Areas of Expertise</b>
Mr. Joe Brobjorg Senior Research Engineer Northern States Power Company	414 Nicollet Mall, RS10 Minneapolis, MN 5540 1 - 1927 Phone: (612) 330-2856 Fax: (612) 330-7671 <i>josephnbrobjorg@nspco.com</i>	Fuel procurement, combustion disposal, and utilization issues.
Mr. Tom Brown Subprogram Manager U.S. Department of Energy Federal Energy Technology Center-Pittsburgh	626 Cochran's Mill Road PO Box 10940, Mail Stop 922-206 Pittsburgh, PA 15236-0940 Phone: (412) 892-4691 Fax: (412) 892-6228 <i>brown@petc.doe.gov</i>	Specializes in projects related to trace elements (especially mercury) and fine particulates (PM <sub>2.5</sub> ). Also serves on many committees and coordinates conference sessions.
Mr. David Johnson Director, Production Otter Tail Power Company	215 South Cascade Street PO Box 496 Fergus Falls, MN 56538-0496 Phone: (218) 739-8399 Fax: (218) 739-8629 Email: <i>djohnson@otpc.com</i>	Fuel procurement combustion disposal and utilization issues.
Ms. Martha Keating Environmental Scientist U.S. Environmental Protection Agency	Research Triangle Park, NC 27711 Phone: (919) 541-5340 Fax: (919) 541-0840	Air toxic inventories, means of control, and emissions from thermal conversion systems.
Dr. Arun K. Mehta Manager, Coal Technology Electric Power Research Institute	Strategic Management Group 3412 Hillview Avenue PO Box 10412 Palo Alto, CA 94303 Phone: (415) 855-2895 Fax: (415) 855-2287 <i>amehta@epri.com</i>	Coal combustion, coal quality effects, combustion chemistry, fate of trace elements.
Mr. Cliff Porter Director and Technical Advisor Lignite Research Council	1016 East Owens Avenue, Suite 200; PO Box 2277 Bismarck, ND 58501 Phone: (701) 258-7117 Fax: (701) 258-2755 <i>cporter@btigate.com</i>	Coal conversion technology.
Mr. David G. Salladay Projects Manager Tennessee Valley Authority	WR 5H, 1101 Market Street Chattanooga, TN 37402 Phone: (423) 751-6359 Fax: (423) 751-2463 <i>dgsalladay@tva.gov</i>	Air toxics control, coal-fired power plants.

***Science Advisory Committee Members***

<b>Member/Affiliation</b>	<b>Address</b>	<b>Areas of Expertise</b>
Mr. Gary Evans J.S. Environmental Protection Agency	Mail Drop 76 Research Triangle Park, NC 27711 Phone: (919) 541-3124 Fax: (919) 541-4046 <i>evans.gary@epamail.epa.gov</i>	Air quality monitoring and data assessment.
Dr. Brian K. Gullett Research Engineer U.S. Environmental Protection Agency	Mail Drop 65 Research Triangle Park, NC 27711 Phone: (919) 541-1534 Fax: (919) 541-0554 <i>bgullett@engineer.aeeri.epa.gov</i>	Halogenated organic pollutant formation and the fate and control of mercury pollutants in combustion systems.
Dr. John N. Harb Associate Professor Brigham Young University	350 CB Provo, UT 84601 Phone: (801) 378-4393 Fax: (801) 378-7799	Modeling and experimental investigation of inorganic transformations, ash formation, and ash deposition in coal-fired systems.
Dr. JoAnn S. Lighty Associate Professor University of Utah	Department of Chemical and Fuels Engineering 3290 MEB Salt Lake City, UT 84112 Phone: (801) 581-5763 Fax: (801) 581-8692	Investigation of the fate of metals during incineration and coal combustion, experimental studies in fluidized-bed combustion, development of a waste incineration system for resource recovery in regenerative life support systems.
Mr. Ed Swain Research Scientist Minnesota Pollution Control Agency	520 Lafayette Road North St. Paul, MN 55155-4194 Phone: (612) 296-7800 Fax: (612) 297-7709 <i>edward.swain@pca.state.mn.us</i>	Ecological impacts of atmospheric deposition on lakes and streams.
Mr. Cliff Twaroski Air Quality Scientist Barr Engineering Company	8300 Norman Center Drive Minneapolis, MN 55437-1206 Phone: (612) 832-2642 Fax: (612) 832-2601 Email: <i>ctwaroski@barr.com</i>	Assessing pollutant emissions transport and environmental fate.

***CATM FUNDING***

<b>Funding Sources</b>	<b>Funds Received 1997</b>	<b>Funds Expended 1997</b>	<b>Funds Expended Through 1997</b>
EPA Core Funding	\$980,000	\$878,903	\$4,085,767
EPA, other	0	0	0
Other Federal <sup>1</sup>	20000	30816	229205
State and Local	20000	7820	127725
Consortium (matching)	0	0	0
Private Sector <sup>2</sup>	132200	165107	584591
<b>Total</b>	<b>\$1,152,200</b>	<b>\$1,082,646</b>	<b>\$5,027,288</b>

<sup>1</sup> Includes complementary funding from DOE.

<sup>2</sup> Includes private sector funding to match DOE complementary funding.

<b>Student Support</b>	<b>1997 Number</b>	<b>1997 Number of Underrepresented Minorities</b>	<b>1997 Funds</b>	<b>Cumulative</b>	
				<b>Number</b>	<b>Funds</b>
Undergraduate	5	0	\$2502	31	\$36,372
Graduate	0	0	0	3	9707
Postdoctoral	0	0	0	4	2637
<b>Total</b>	<b>5</b>	<b>0</b>	<b>\$2502</b>	<b>38</b>	<b>\$48,716</b>

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One-Day Short Course on "Trace Metals in Industrial Applications," held at Northern States Power Company, Minneapolis, MN, Sept. 20, 1996.

The Second International Conference on Energy and Environment: Transitions in East Central Europe, Prague, Czech Republic, Nov. 1-5, 1994; cosponsored by the Energy & Environmental Research Center, Grand Forks, ND, USA, and EGÚ Prague, PLC, Prague, Czech Republic.

Two-Day Workshop on Least-Cost Economic Power Generation in East Central Europe, Oct. 31–Nov. 1, 1994; held in coordination with the Second International Conference on Energy and Environment: Transitions in East Central Europe, Prague, Czech Republic.

Two-Day Workshop on Production and Utilization of Ecological Fuels from East Central European Coals, Oct. 31 – Nov. 1, 1994, held in coordination with the Second International Conference on Energy and Environment: Transitions in East Central Europe, Prague, Czech Republic.

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*CATM Newsletter Articles*

*CATMNewsletter*, January 1997, Volume 3, Issue 1:

- Trace Element Transformations During Oil Combustion
- Director's Message: CATM Third Annual Meeting
- Technical Focus: Transformation and Partitioning of Trace Elements During Combustion
- DOE Addresses Industry Needs Regarding Air Toxic Issues (part 2)
- Thermal Decomposition Process Applied to Volume Reduction of Radioactive Organic Waste
- EPA Assistant Administrator Visits the EERC
  - Trace Metals Short Course
  - CATM Database Now Available Via Internet
  - DOE Phase I Field Test Assessment Available

*CATM Newsletter*, June 1996, Volume 2, Issue 2:

- Mercury Speciation Measurement Project Continuing at the EERC
- Director's Message: Where We're Going in 1997
- Technical Focus: CATM Air Toxic Metals Database Available
- DOE Addresses Industry Needs Regarding Air Toxic Issues (part 1)
- EERC's New Mercury Laboratory Supports Multiple Projects
- EPA Assistant Administrator Visits the EERC
  - Update on Status of EPA "Reports to Congress"
  - CATM Communique

*CATMNewsletter*, December 1995, Volume 2, Issue 1:

- Phase I Trace Element Results from the DOE Toxic Emissions Field Study
- Director's Message: CATM Second Annual Meeting
- Technical Focus: Hazardous Air Pollutant Correlations Evaluated for DOE
- Mercury Workshops Sponsored by GRI and DOE
- Construction of New Intermediate-Scale Combustion Test Facility Nears Completion
- EPA Assistant Administrator Visits the EERC
  - CATM Communique

*CATMNewsletter*, Spring 1995, Volume 1, Issue 3:

- Industry and Government Team to Test Methods to Mitigate Metal Emissions
- Director's Message: New Initiatives in CATM
- Technical Focus: On-Line Analysis of Mercury
- Mercury in the Environment: Soils
- EERC and DOE Review Air Toxic Emissions Data from Advanced Power Systems
- Jack Pirkey Elected CATM Science Advisory Committee Chair

- CATM Annual Report Available
- On-Line Mercury Monitor Evaluation
- CATM Communique

*CATM Newsletter*, Fall/Winter 1994, Volume 1, Issue 2:

- EERC Meets with Industry, EPA and DOE Representatives on Air Toxic Metals
- Director's Message: The Energy & Environmental Research Center and the Center for Air Toxic Metals
- Technical Focus: Research Points Way to Enhanced Air Toxics Control
- "Partnerships for a Better Quality of Life" – CATM Cosponsors Second International Conference in Czech Republic
- Energy Secretary O'Leary Dedicates New EERC Research and Laboratory Additions
- Verification Tests for Mercury Speciation Using EPA (Draft) Method 29
  - HAP Emissions from Advanced Power Systems: A Full-Scale Examination
  - CATM Communique
  - On-Line Mercury Analyzer

*CATM Newsletter*, Summer 1994, Volume 1, Issue 1:

- Center for Air Toxic Metals Hosts First Annual Meeting
- Director's Message: CATM: Providing Partnership Opportunities
- Technical Focus: CATM Database: A New Tool for Air Toxics R&D
- CATM Works with DOE to Review and Assess Air Toxic Emissions from Coal-Fired Power Plants
- Dalway Swaine Joins the EERC and CATM Team
  - Trace Elements Workshop: Special Issue Due for Release
  - Database Participation
  - New Test Facility Designed for Determining Trace Metals Behavior and Control

